This is a reproduction of a library book that was digitized by Google as part of an ongoing effort to preserve the information in books and make it universally accessible.

Google™ books

https://books.google.com

F VIRGINIA LIBRARY
783784

ALDERMAN LIBRARY
UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

CONDUCTED BY

SIR OLIVER JOSEPH LODGE, D.Sc., LL.D., F.R.S.
SIR JOSEPH JOHN THOMSON, O.M., M.A., Sc.D., LL.D., F.R.S.
JOHN JOLY, M.A., D.Sc., F.R.S., F.G.S.
RICHARD TAUNTON FRANCIS, F.R.S.E.
AND
WILLIAM FRANCIS, F.L.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. Polit. lib. i. cap. 1. Not.

VOL. II.—SEVENTH SERIES.

JULY—DECEMBER 1926.

LONDON:

TAYLOR AND FRANCIS, RED LION COURT, FLEET STREET.

SOLD BY SMITH AND SON, GLASGOW;—HODGES, FIGGIS, AND CO., DUBLIN;—
AND VEUVE J. BOYVEAU, PARIS.

UNIVERSITY OF VIRGINIA GENERAL LIBRARY 1819

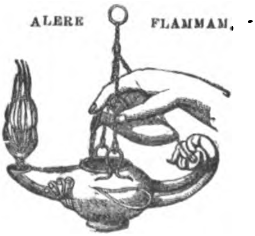
u V2 4

Q
1
.P5
099263
7th ser.
v.2
1926

"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.



CONTENTS OF VOL. II.

(SEVENTH SERIES).

NUMBER VII.—JULY 1926.

Page

Mr. T. I. Edwards on the Resistivity and Conductivity of Dilute Amalgams at various Temperatures........................... 1

Mr. W. Sucksmith on the Magnetic Susceptibilities of some Alkalis. 21

Prof. F. Ehrenhaft and Dr. E. Wasser on Determination of the Size and Weight of Single Submicroscopic Spheres of the Order of Magnitude $r=4.10^{-5}$ cm. to 5.10^{-6} cm., as well as the Production of Real Images of Submicroscopic Particles by means of Ultraviolet Light. (Plate I.)........................... 30

Dr. A. H. Davis and Mr. N. Fleming on the Loud-Speaker as a Source of Sound for Reverberation Work............................ 51

Mr. R. M. Wilmotte on the Calculation and Application of High Resistances of small Self-Inductance for all Frequencies........ 65

Dr. L. C. Jackson on Atomic Structure and the Magnetic Properties of Coordination Compounds.............................. 86

Dr. E. C. Stoner on X-Ray Term Values, Absorption Limits, and Critical Potentials................................... 97

Dr. E. C. S. Dickson and Mr. W. Binks on the Crystalline Structure of Anhydrite.................................... 114

Messrs. E. W. B. Gill and R. H. Donaldson on a New Method of obtaining a Luminous Discharge in Gases at very Low Pressures. 129

Mr. T. Carlton Sutton on Shape of Waves from Large Explosions .. 137

Dr. H. Banister on the Transmission of Sound through the Head... 144

Dr. E. Hughes on Minimization of Magnetic Leakage and of its Effect in the Magnetic Testing of Bars and Rods............... 162

Miss P. Jones and Mr. T. J. Jones on the Effect of a Magnetic Field on the Electrical Resistance of Mercury and some Amalgams..... 176

Prof. W. M. Hicks on the Analysis of the Copper Spectrum....... 194

Dr. J. Kunz on the Fluctuation Theory of Scattering of Light in Gases...................................... 237

Dr. H. Jeffreys on the relation to Physics of the notion of Convergence of Series............................... 241

Prof. J. Joly on Professor Lees' Criticism of 'The Surface History of the Earth'................................. 245

Dr. P. J. Daniell on Orthogonal Potentials.................... 247

Prof. W. L. Bragg on Interatomic Distances in Crystals........... 258

Mr. T. L. Eckersley on the Compton Scattering and the Structure of Radiation................................. 267

Dr J. A. Wilcken on the Molecular Association of Benzoic Acid in Benzene.................................. 287

Dr. F. S. Goucher on Further Studies on the Deformation of Tungsten Single Crystals. (Plates II.–V.)................ 289

Page

Prof. R. W. Wood and Mr. T. Lyman on Improved Grating for Vacuum Spectrographs. (Plate VI.) 310

Prof. A. Grumbach on the Origin of the E.M.F. of a Photoelectric Cell containing a Fluorescent Electrolyte 313

Dr. R. Winstanley Lunt on the Determination of the Current Voltage Characteristic of a Siemens Ozonizer 314

Prof. H. P. Waran on a simple Vacuum Arc Mercury Still for Laboratories 317

NUMBER VIII.—AUGUST.

Messrs. E. Edwards, I. Bowen, and S. Alty on the Effect of Tension on certain Elastic Properties of Wires. (Plate VII.) 321

Mr. L. L. Bircumshaw on the Surface Tension of Liquid Metals.—Part I. Tin and Lead 341

Mr. H. W. Swift: Determination of the Modulus of Elasticity by Dynamical Methods 351

Dr. N. R. Campbell on the Variation of Pressure with Temperature in Evacuated Vessels 369

Mr. W. H. Patterson on a Bath for Observations at Lower Temperatures 383

Mr. M. F. Carroll on Molecular Association and the Equation of State 385

Dr. H. Banister on Phase-effect and the Localization of Sound: an Examination of the Myers-Wilson Hypothesis 402

Prof. A. Press on the Elasticity Coefficients and the Thermodynamic Integration Factor for the Solid State 431

Mr. E. Tyler and Dr. E. G. Richardson on Eddying Flow from Annular Nozzles 436

Mr. S. E. Sheppard on some Considerations of the Reaction Constant Equation, and a Simple Method of Determining the End Point .. 448

Mr. A. M. Binnie on Temperature Stresses and Deflexions in the Fins and Barrel of an Air-cooled Internal Combustion Engine Cylinder. 449

Dr. L. A. Welo on the Photoelectric Emission from Platinum as Influenced by Heating 463

Prof. J. S. Townsend and Mr. C. M. Focken on the Transference of Energy in Collisions between Electrons and Molecules 474

Notices respecting New Books:—
- Mr. L. B. W. Jolly's Summation of Series 496
- Messrs. Kaye and Laby's Four-figure Mathematical Tables.... 496
- Sir Jagadis Chunder Bose's The Nervous Mechanism of Plants. 496

NUMBER IX.—SEPTEMBER.

Dr. G. Green on the Condenser-Telephone 497

Mr. R. C. Richards on the High Frequency Oscillatory Discharge in Rarefied Gas. (Plate VIII.) 508

Dr. R. A. Houstoun on the Theory of the Absorption of X-Rays .. 512

Dr. R. C. Gray on the Magnetic Stability of Permanent Magnets.. 521

Page
Dr. W. H. McCurdy on Absorption and Resonance Radiation in Excited Helium and the Structure of the 3889 Line. (Plate IX.) 529
Mr. E. A. Guggenheim on the Determination of the Velocity Constant of a Unimolecular Reaction 538
Dr. A. H. Davis on the Basis of Acoustic Measurements by Reverberation Methods 543
Mr. W. Stephenson on the Effect of the Shape of the Cathode on the Glow Discharge 556
Dr. G. Scatchard on the Milner and Debye Theories of Strong Electrolytes 577
Messrs. G. Nonhebel and H. Hartley on the Milner and Debye Theories of Strong Electrolytes 586
Mr. R. F. Gwyther on a Geometrical Presentment of the Constants of an Elastic Material 588
Mrs. M. R. Johnson and Dr. R. C. Johnson on Intensity Variations in the Spectrum of Neon. (Plate X.) 593
Prof. R. W. Wood: Note on the Structure of Cadmium and Zinc Resonance Lines. (Plate XI.) 611
Mr. W. A. MacNair on the Fine Structure of Certain Lines and Energy Levels of Radium. (Plate XII.) 613
Dr. R. C. Johnson and Mr. H. G. Jenkins: Note on some Observations of the Nitrogen Afterglow Spectra 621
Mr. N. K. Sur on the Arc Spectrum of Lead 633
Prof. C. G. Barkla and Dr. S. R. Khastgir on Scattered X-Rays. The J Phenomenon (Part IV.) 642
Mr. E. J. Williams on the Compton Effect and the Reflexion of X-Rays by Crystals 657
Sir J. J. Thomson on Radiation produced by the Passage of Electricity through Gases 674
Mr. Y. Björnstahl on Electric Double Refraction in Colloids. (Plate XIII.) 701
Mr. V. H. L. Searle on an Oscillographic Study of Anodic Polarization 733
Dr. F. Kirchner on a New Method of obtaining a Luminous Discharge in Gases at very Low Pressures 741
Messrs. E. W. B. Gill and R. H. Donaldson on a New Method of obtaining a Luminous Discharge in Gases at very Low Pressures. 742
Mr. A. K. Sur on the Water-Spark Absorption Spectrum of Iron .. 742
Dr. Winstanley Lunt on a New Method of Producing a Discharge in Hydrogen 743
Proceedings of the Geological Society:—
  Mr. V. G. Glenday and Dr. J. Parkinson on the Geology of the Suk Hills (Kenya Colony) 744
  Mr. T. O. Morris and Prof. W. G. Fearnsides on the Stratigraphy and Structure of the Cambrian Slate-Belt of Nantlle (Carnarvonshire) 744
  Prof. S. J. Shand on the Alkaline Rocks and Ring-Intrusions of Pilansberg (Transvaal) 747
  Dr. J. W. Evans on Regions of Compression 748
  Dr. G. L. Elles on the Geological Structure of Ben Lawers and Meall Corranaich (Perthshire) 749
  Prof. J. E. Marr on the Pleistocene Deposits of the Lower Part of the Great Ouse Basin 750

NUMBER X.—OCTOBER.

Page

Dr. E. T. Paris on the Theory of the "Boys" type of Double Resonator 751

Mr. C. S. Beals on Regularities in the Spectrum of Ionized Silver. (Plate XIV.) 770

Dr. A. A. Robb on a Simple Integraph 778

Dr. L. H. Clark on Secondary Radiations produced by Gamma Rays and their Effect upon Gamma-Ray Absorption Measurements 783

Prof. F. H. Newman on the High Vacuum Arc in Hydrogen. (Plate XV.) 796

Prof. W. B. Morton on the Action in Parabolic Paths under Gravity. 800

Mr. J. S. Rankin on the Elastic Range of Friction 806

Mr. G. W. C. Yates on Latent Heats of Vaporization of Ethyl and Methyl Chlorides 817

Prof. W. B. Morton on the Parallel-Plate Condenser and other Two-Dimensional Fields Specified by Elliptic Functions 827

Dr. H. Jeffreys on the Stability of a Layer of Fluid heated below .. 833

Prof. H. Levy on Growth of Eddies in a Viscous Fluid 844

Mr. H. W. Swift on Orifice Flow as affected by Viscosity and Capillarity 852

Prof. R. W. Wood on Self-Reversal of the Red Hydrogen Line 876

NUMBER XI.—NOVEMBER.

Mr. E. Ower on the Theory of the Vane Anemometer 881

Prof. W. B. Morton on Irrotational Flow past Two Intersecting Planes 900

Rev. P. J. Kirby on Alternative Currents in Rarefied Oxygen in the same Circuit 913

Mr. J. P. Andrews on an Application of Diffraction Halos to Elasticity 945

Mr. B. M. Cassen on the Striated Distribution of Space Charge ... 948

Dr. H. M. Browning on Sound Changes analysed by Records.—II. Voice and Violin. (Plate XVI.) 955

Mr. N. Eumorfopoulos and Lieut. J. Rai on the Joule-Thomson Effect for Air 961

Prof. T. R. Merton on Reversal in Vacuum Tube Spectra 975

Dr. B. van der Pol, Jun., on "Relaxation-Oscillations" 978

Prof. J. A. Wasastjerna on the Crystalline Structure of Anhydrite. 992

Mr. D. Meksyn on Equilibrium and Motion of a Continuous Medium in Four-dimensional Space 994

Mr. R. Thoræus on the X-Ray Spectra of the Lower Elements. (Plates XVII. & XVIII.) 1007

Mr. W. W. Barkas on Photophoresis of Colloidal Particles in Aqueous Solutions (Plate XIX.) 1019

Dr. S. H. C. Briggs on Werner's Co-ordination Theory and the Electrical Structure of the Atom. The Relationship between Valency and Co-ordination 1026

Prof. F. H. Newman on the Flash Arc Spectrum of Potassium. (Plate XX.) 1042

Dr. A. Dauvillier: Researches on the Electric Discharge in Gases and the accompanying Radiation 1046

Mr. H. F. Biggs on a Simple Exposition of Electromagnetic Relations 1052

Dr. J. Chadwick: Observations concerning the Artificial Disintegration of Elements 1056

Prof. G. P. Thomson on Scattering of Positive Rays by Gases.—II. 1076

Mr. G. Nonhebel on the Activity Coefficients of Aqueous Hydrochloric Acid at Extreme Dilutions 1085

Page
Messrs. R. C. J. Howland and T. W. Dickson on the Oblique Rebound of a Ball from a Fixed Plane 1091
Mr. R. M. Wilmotte: General Formulæ for Two Syntonized Coupled Circuits 1098
Messrs. J. M. Nuttall and E. J. Williams on the Ranges of Secondary β-Rays 1109
Prof. C. G. Barkla and Miss G. I. Mackenzie: Notes on Scattered X-Rays. The J Phenomenon. (Part V.) 1116
Prof. C. G. Barkla and Dr. W. H. Watson on the Control of the J Phenomenon (Part VI.) 1122
Dr. J. H. Shaxby on the Density of Fluids.—I. On a Relation between Density and Temperature and on the Latent Heat of Vaporization 1127
Prof. E. T. Whittaker on a Simple Light-Quantum 1137
Dr. W. E. Adeney on the Rate and Mechanism of the Aeration of Water under Open-Air Conditions 1140
Prof. H. Perlitz on an Apparent Relation between the Rate in the Change of the Electric Resistance at Fusion and the Crystal Lattice of Metallic Elements 1148

NUMBER XII.—DECEMBER.

Dr. A. Nath Sarkar on an X-ray Examination of the Crystal Structure of Certain Compounds. (Plates XXI. & XXII.) 1153
Dr. J. S. Owens on the Making of a Salt Haze 1165
Prof. P. Lasareff on the General Theory of the Sensation of Flickers in Peripheral and Central Vision 1170
Mr. H. V. Lowry on the Legendre Function of Order $-\frac{1}{2}$ 1184
Dr. A. L. Norbury on the Thermoelectric Properties of Certain Metallic Solid Solutions 1188
Dr. R. Chaplin on the Adsorption of Nitrogen at Low Pressures by Activated Charcoal 1198
Prof. N. P. Kasterin on Sir J. J. Thomson's Model of a Light-Quantum 1208
Prof. R. R. Ramsey on the Resistance of High-Frequency Circuits. 1213
Drs. A. Holmes and R. W. Lawson on the Radioactivity of Potassium and its Geological Significance 1218
Prof. A. J. S. Pippard and Mr. J. F. Baker on the Stresses in a Spoked Wheel under Loads applied to the Rim 1234
Dr. A. C. Davies and Prof. F. Horton on Critical Potentials and X-ray Term Values 1253
Dr. P. W. Bridgman on Dimensional Analysis Again 1263
Dr. E. A. Owen and Mr. G. D. Preston on the Atomic Structure of AgMg and AuZn 1266
Mr. B. S. Cohen on the Condenser-Telephone 1271
Dr. F. Kirchner on Luminous Discharge in a Rapidly Alternating Field 1272
Mr. A. W. Barton on the Existence and Half-Period of Radium C. 1273
Mr. M. Hart on the Loud-Speaker as a Source of Sound for Reverberation Work 1282
Notices respecting New Books:—
  Dr. A. C. Crehore's The Progress of Atomic Theory 1284
  Mr. T. L. Heath's The Thirteen Books of Euclid's Elements.. 1284
  Mr. C. V. Durell's Projective Geometry 1285
  Mr. S. L. Loney's Solutions of the Examples in a Treatise on Dynamics of a Particle and of Rigid Bodies 1285
  Messrs. G. M. B. Dobson, I. O. Griffith, and D. N. Harrison's Photographic Photometry 1286
  Mr. R. T. Gunther's Early Medicine and Biological Sciences.. 1286

Page
Proceedings of the Geological Society :—
Mr. R. M. Jehu on the Geology of the District around Towyn and Abergynolwyn (Merioneth)........................ 1287
Index 1288

PLATES.

I. Illustrative of Prof. F. Ehrenhaft and Dr. E. Wasser's Paper on Determination of the Size and Weight of Single Submicroscopic Spheres of the Order of Magnitude $r=4 . 10^{-5}$ cm. to $5 . 10^{-6}$ cm., as well as the Production of Real Images of Submicroscopic Particles by means of Ultraviolet Light.
II.-V. Illustrative of Dr. F. S. Goucher's Paper on Further Studies on the Deformation of Tungsten Single Crystals.
VI. Illustrative of Prof. R. W. Wood and Mr. T. Lyman's Paper on Improved Grating for Vacuum Spectrographs.
VII. Illustrative of Messrs. E. Edwards, I. Bowen, and S. Alty's Paper on the Effect of Tension on certain Elastic Properties of Wires.
VIII. Illustrative of Mr. R. C. Richards's Paper on the High Frequency Oscillatory Discharge in Rarefied Gas.
IX. Illustrative of Dr. W. H. McCurdy's Paper on Absorption and Resonance Radiation in Excited Helium and the Structure of the 3889 Line.
X. Illustrative of Mrs. M. R. Johnson and Dr. R. C. Johnson's Paper on Intensity Variations in the Spectrum of Neon.
XI. Illustrative of Prof. R. W. Wood's Paper on the Structure of Cadmium and Zinc Resonance Lines.
XII. Illustrative of Mr. W. A. MacNair's Paper on the Fine Structure of Certain Lines and Energy Levels of Cadmium.
XIII. Illustrative of Mr. Y. Björnstahl's Paper on Electric Double Refraction in Colloids.
XIV. Illustrative of Mr. C. S. Beals's Paper on Regularities in the Spectrum of Ionized Silver.
XV. Illustrative of Prof. F. H. Newman's Paper on the High Vacuum Arc in Hydrogen.
XVI. Illustrative of Dr. H. M. Browning's Paper on Sound Changes analysed by Records.
XVII. & XVIII. Illustrative of Mr. Thoræus's Paper on the X-Ray Spectra of the Lower Elements.
XIX. Illustrative of Mr. W. W. Barkas's Paper on Photophoresis of Colloidal Particles in Aqueous Solutions.
XX. Illustrative of Prof. F. H. Newman's Paper on the Flash Arc Spectrum of Potassium.
XXI. & XXII. Illustrative of Dr. A. N. Sarkar's Paper on an X-Ray Examination of the Crystal Structure of certain Compounds.

ERRATUM.

August Number: the last line page 342 and the first line page 343 should read "the mean diameter being 1·016 M.M.," not 1·016 cms.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

JULY 1926.

I. *The Resistivity and Conductivity of Dilute Amalgams at various Temperatures.*

By T. I. EDWARDS, *M.Sc.*, *Research Student, University College of Swansea* [*].

INTRODUCTION.

THE work described in this paper is a continuation of that carried out by E. J. Williams [†], who determined accurately the conductivities of mercury, and dilute amalgams of cadmium, indium, and magnesium at temperatures ranging from 0° C. to 300° C.

Although a large number of observations have been carried out by various workers on the conductivities of several amalgams the results are not always in agreement, and, in addition, there are still some amalgams whose conductivities at different temperatures have not been investigated.

The present investigation deals with amalgams of thallium, germanium, antimony, yttrium, cerium, aluminium, and beryllium, and the results are examined in relation to a theory put forward by Skaupy [‡].

It is a well-known experimental fact that the conductivity of liquid mercury is, in general, increased by the addition of even small quantities of metals such as zinc, cadmium, and lead. The results are in marked contrast to those obtained with homogeneous solid solutions where the conductivity is lowered, and cannot be attributed to the difference between liquid and solid as is shown by the fact that certain dilute alkali amalgams are poorer conductors than pure mercury.

---

[*] Communicated by Prof. E. J. Evans, D.Sc.

[†] Phil. Mag. Sept. 1925, p. 589.

[‡] Skaupy, *Zeit. für Physik. Chemie*, lxviii. p. 560 (1907); *Verhd. Deut. Phys. Ges.* xvi. p. 156 (1914); *Ibid.* xviii. p. 252 (1916); *Phys. Zeit.* xxi. p. 597 (1920).

Skaupy bases his theory on an analogy between liquid metals and electrolytic solutions, and assumes that the electrical conductivity of a pure solvent must be expressed as a function of the concentration of electrons and of internal friction.

He further assumes that dilute metallic solutions must show a higher electron concentration than the solvent, as splitting off of electrons occurs when the dissolved substance dissociates, and also that chemical relations of equilibrium must exist between solvent and matter dissolved, as both possess a common ion in the negative electron.

The conductivity L of a metallic liquid is proportional to the electron concentration ϵ, and inversely proportional to the internal friction (viscosity) η, and this can be written

$$\epsilon = \text{constant} \,.\, L \,.\, \eta \qquad (1)$$

Taking logarithms of both sides of the equation and differentiating, we obtain :

$$\frac{1}{\epsilon}\Delta\epsilon = \frac{1}{L}\Delta L + \frac{1}{\eta}\Delta\eta \qquad (2)$$

Let c = concentration of substance dissolved in mercury expressed in gram atoms per 100 gram atoms of mercury, *i. e.*, approximately in atom atoms per cent.

Dividing by c, equation (2) becomes

$$\frac{1}{\epsilon}\frac{\Delta\epsilon}{c} = \frac{1}{L}\frac{\Delta L}{c} + \frac{1}{\eta}\frac{\Delta\eta}{c} \qquad (3)$$

Δ expresses that we are dealing with finite changes however small, corresponding to small but finite concentrations, and we can substitute for L and η suitable corresponding values for the pure solvent.

Putting

$$\frac{1}{\epsilon}\frac{\Delta\epsilon}{c} = H\,;\quad \frac{1}{L}\frac{\Delta L}{c} = l, \text{ and } \frac{1}{\eta}\frac{\Delta\eta}{c} = r,$$

we obtain from (3)

$$H = l + r,$$

which for infinite dilution can be expressed as

$$H_\infty = l_\infty + r_\infty \qquad (4)$$

Skaupy showed in his first paper that l_∞ has approximately the same value for a number of metals dissolved in mercury.

The rule that l_∞ is approximately constant for different metals does not hold in the case of some alkali amalgams, and the difficulty was not removed until Feninger's * work showed the increased value of the viscosity for these amalgams. If this is taken into account, we obtain the more general rule that

$$H_\infty = l_\infty + r_\infty$$

should have the same order of magnitude for different metals dissolved in mercury.

Another point of interest discussed by Skaupy is the variation of H with concentration. It can be shown that $\frac{H_\infty - H}{c}$ must be constant; but, as the variation of internal friction with increase of concentration is not sufficiently known, one is often obliged to consider the values of $\frac{l_\infty - l}{c}$ in the case of amalgams in which the change of internal friction is not so great as in the alkali metals.

In the present paper the values of l_∞ and $\frac{l_\infty - l}{c} = K$ will be discussed for the amalgams examined.

The metals used in these experiments were supplied by Messrs. Harrington Bros. and were the purest they could procure. In the case of both thallium and cerium, two specimens obtained from different sources were employed and the results were found to be identical. The germanium was obtained from Dr. Schuchardt, Görlitz. It is, however, difficult to be certain about the state of purity of yttrium.

Before the experiments on amalgam were commenced, the work of Williams on the conductivity of mercury at various temperatures from 0° C. to 300° C. was repeated in a quartz tube, so as to minimise as far as possible the corrections that must be applied due to the expansion of the containing vessel.

EXPERIMENTAL ARRANGEMENT.

The resistance of a fine column of liquid contained in a capillary tube (as shown in fig. 1) was measured by means of a Callendar and Griffiths Bridge, and a high sensitivity galvanometer which gave a deflexion of 1 mm. on a scale 1 metre away when a current of $2{\cdot}5 \times 10^{-9}$ ampere was passed through it. With the bridge used the resistance could be estimated to ·00005 ohm, this corresponding to a change of temperature of ·05° C.

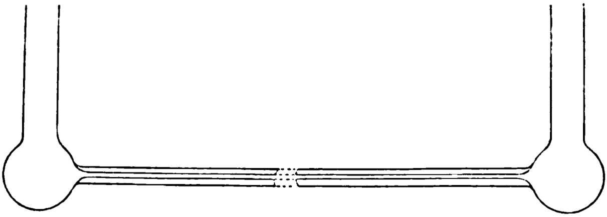
The various resistances of the bridge were known in

---

* H. Feninger, 'Die Electrische Leitfähigkeit und innere Reibung Verdünntner Amalgame,' Freiburg, 1914.

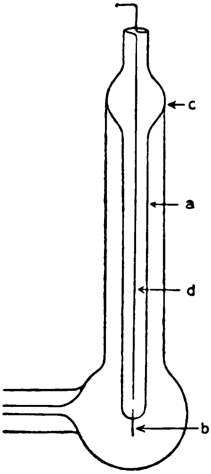
relation to one another, so as to be able to determine the relative changes of the resistances measured. A knowledge of the correct absolute values of the bridge resistances is not necessary for an accurate determination of the temperature coefficient of resistivity of mercury or amalgam, as long as their relative values are known accurately. Even in the case of the absolute determinations of resistivity of mercury and amalgams the absolute value of the bridge resistances is not required as the resistivity of mercury at 0° C. is taken to be 94074 × 10^9, and this corresponds to a known value of the resistance for a given tube.

Fig. 1.



The liquid whose resistance was to be measured was placed in a capillary tube which opened out at both ends into wide limbs at right angles to the capillary.

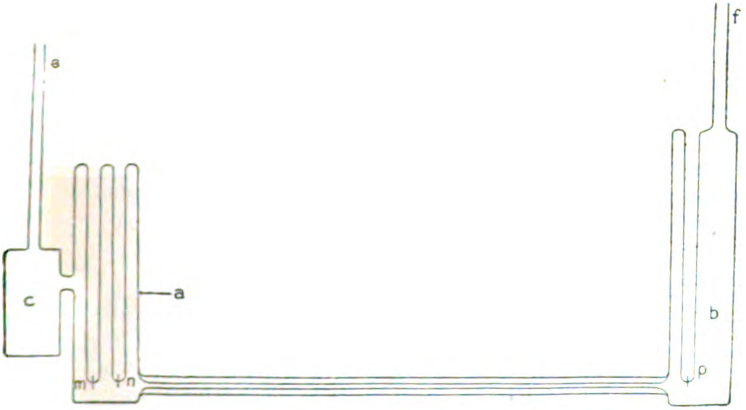
Fig. 2.



Glass tubes or leads (*a*), fig. 2, into which platinum wires (*b*) were sealed, fitted into the limbs. The leads were held in position by ground-glass joints at (*c*), and were about half-filled with mercury, into which were placed copper wires (*d*), the length of wire immersed being always the same so that the resistances of the leads were always the same at the same temperature. The copper wires were connected to the bridge by flexible wires, and in order to eliminate any change in the resistance of the wires during an experiment, a pair of flexible compensating wires were also connected to the bridge. The resistances between the platinum points when the leads were, firstly, in the same cup of mercury and, secondly, in the limbs of the capillary tube, were measured in every determination, and the difference between these resistances was taken as the resistance of the mercury in the capillary tube.

For metals which oxidize in amalgams a tube which could be evacuated (fig. 3) was used.

Fig. 3.



The side limbs "a" and "b" were fused on to the capillary, and to "a" was fused another side vessel "c." The tube was open to the air at "e" and "f." Platinum points were sealed on to the leads "m." "n," and "p," which were fixed in the tube. The tube was thoroughly cleaned and dried, mercury placed in "b" and the metal was added at "e," so as to remain in the side vessel "c" separate from the mercury. The tube was connected to a Töpler pump and a bulb containing phosphorus pentoxide and then evacuated to a pressure of ·01 mm., the pressure being measured by means of a McLeod gauge. Dry hydrogen was then allowed to pass into the tube to a pressure sufficient to give one atmosphere at the highest temperature at which the resistance was to be measured. The tube was then sealed off at "e" and "f," and the mercury allowed to run into the vessel "c" on to the metal. When the metal had completely dissolved, the amalgam was poured back into the capillary and the measurements made. The resistance of the tube, containing pure mercury, was determined at different temperatures, and by comparing the values of the temperature coefficient with the corrected values obtained with the quartz tube, the correction for the expansion of the glass was found.

The resistance of the liquid in the capillary was taken as the difference between the resistances when the leads were firstly in "n" and "p," and secondly in "m" and "n."

Thermoelectric Currents.

When the galvanometer circuit was closed, a deflexion of the mirror was produced by thermoelectric currents, and the point of balance on the bridge could not be found by the usual method. To overcome this difficulty, the galvanometer arm was always kept closed and the bridge was adjusted so that there was no change of deflexion of the galvanometer mirror on completing the battery circuit. When this condition was obtained, the value of the resistance is the correct one in virtue of the properties of conjugate conductors.

Method of Heating and of Measuring Temperature.

For measuring the resistance at 0° C. the tube and mercury cup were immersed in a bath of melting ice, and for measurements at room temperature a water-bath was used. For higher temperatures a bath of vigorously boiling liquid, of an appropriate boiling-point, was used. The following liquids, having the specified boiling-points, were used:—Water (100° C.); aniline (184° C.); eugenol (256° C.); diphenylamine (300° C.).

It was found that the temperatures of the boiling liquids increased with continued heating, until a steady temperature was reached. Observations were not made until this constant temperature was reached; a series of measurements of temperature, and of the resistance with the leads in the same column of liquid (cup A, fig. 4) and in the tube, were taken to ensure constant results. The resistances were found to be constant to within ·0001 ohm.

The possible error in each of these measurements was less than ·0001 ohm, so that the possible error in the resistances of the liquid was less than ·0002 ohm.

The temperature was measured by means of a platinum resistance thermometer and a set of mercury thermometers. The platinum thermometer was calibrated in melting ice, steam, and the vapour of boiling mercury, and the constant δ in the equation

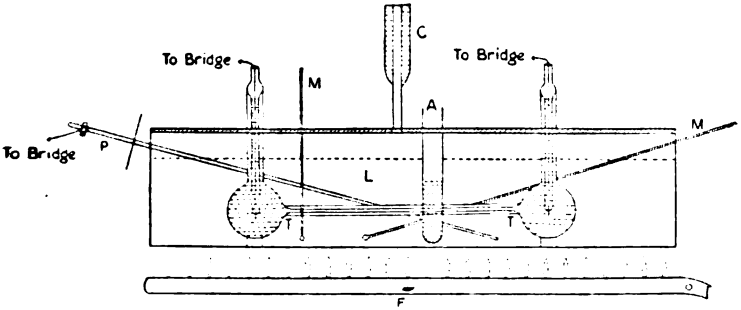
$$t - t_{pt} = \delta\left\{\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right\}$$

was found to be 1·51.

The mercury thermometers, covering a range 0° C. to 300° C., were calibrated against the platinum thermometer.

Fig. 4 shows the arrangement of the thermometers and tube in the bath.

Fig. 4.



T = Tube containing mercury or amalgam.
A = Cup containing mercury or amalgam.
P = Platinum thermometer.
M = Mercury thermometers.
L = Liquid to be boiled.
C = Reflux condenser.
F = Burner.

The formation of bubbles in the capillary tube, especially at high temperature, was a source of much trouble. To avoid this, the tube and mercury were separately heated to the boiling-point of mercury, and the hot mercury added to the tube. Both were then heated to a temperature above that at which the resistance was to be measured, and the tube was carefully examined for bubbles by means of a lens, and any bubbles left were removed.

After each determination at a high temperature, the resistance of the mercury was measured after it had cooled to room temperature, and if this value was correct it was assumed that no bubbles had formed at the high temperature.

EXPERIMENTAL RESULTS.

E. J. Williams[*] determined the temperature coefficient of the electrical resistance of mercury between 0° C. and 300° C., using a glass tube, and applied corrections due to the expansion of the glass on heating. These corrections were of the order of 1 per cent., and involved the determination of the average coefficient of linear expansion of the glass envelope over certain ranges of temperature. Owing to the difficulty of measuring the coefficient of expansion accurately, and its comparatively rapid rise with temperature, it was considered advisable to repeat the experiments with mercury under conditions which made the corrections for the expansion of the containing envelope of far less consequence.

For this purpose, the mercury was contained in a tube (fig. 1) of fused quartz of diam. 1 mm. and length about 37 cm., giving a resistance at 0° C. of about 0·5 ohm.

The value of the coefficient of linear expansion of fused quartz was taken from Kaye and Laby's Tables of Physical and Chemical Constants[†]. The values given are :—

$$\cdot 50 \times 10^{-6} \text{ over the range } 0^\circ \text{ C. to } 100^\circ \text{ C.,}$$

and

$$\cdot 54 \times 10^{-6} \text{ over the range } 0^\circ \text{ C. to } 1000^\circ \text{ C.}$$

The results obtained for mercury in the quartz tube are given in Table I.

The temperature coefficient of resistance of a column of mercury of constant dimensions is the same as the temperature coefficient of the resistivity of mercury. The former is given in column 5, and the resistivities of mercury at various temperatures are given in column 6, the resistivity at 0° C. being assumed to be $94{\cdot}074 \times 10^{-6}$, and the values at the different temperatures being calculated from the corrected values of the average temperature coefficient given in column 5. The conductivity of mercury at the various temperatures is given in the last column. The percentage probable error in the resistivity and conductivity is estimated to be on the average about ·02.

The resistivity over the range of temperatures examined can be represented by the equation

$$\rho = \rho_0(1 + at + bt^2 + ct^3),$$

where ρ_0 is the resistivity at 0° C. and a, b, and c are constants.

---

[*] *Loc. cit.*

[†] Kaye and Laby's 'Tables of Physical and Chemical Constants,' p. 53.

TABLE I.

Temperature in degrees centi-grade.	Resistance in ohms.	Average temperature coefficient of resistance for the range 0° C. to t° C. (uncorrected for expansion of quartz) × 10⁴.	Correction due to expansion of quartz = $+\frac{R}{R_0}g \times 10^4$.*	Corrected average temperature coefficient of resistance for the range 0° C. to t° C.	Resistivity at t° C. × 10⁹.	Conductivity at t° C. × 10¹.
0	·49500	......	......	......	94074	106300
14·8	·50160	9·009	·005	9·014	95328	104901
100	·54385	9·868	·005	9·873	103361	96749
168·9	·58330	10·561	·006	10·567	110863	90201
255·5	·64080	11·528	·006	11·534	121797	821038
300	·67275	11·970	·007	11·977	127876	78201

* R is the observed resistance of mercury filling the capillary at a temperature t° C.; R_0 is the resistance at 0° C., and "g" the average coefficient of linear expansion of the glass from 0° C. to t° C.

The values of the constants a, b, and c, which represent with great accuracy the variation of resistivity with temperature, are:

$$a = \cdot 0_3 8877,$$

$$b = \cdot 0_6 977,$$

$$c = \cdot 0_9 19.$$

The variation of resistivity of mercury with temperature is therefore given by the equation:

$$\rho_t = \rho_0 \{1 + \cdot 0_3 8877\, t + \cdot 0_6 977\, t^2 + \cdot 0_9 19\, t^3\},$$

and the values of the resistivity calculated from the formula agree with those determined experimentally within about ·02 per cent. on the average.

It is not proposed here to compare the results obtained in the present experiments with those obtained by other investigators*, except to point out that the values of the resistivity and conductivity are in good agreement with those obtained by Williams, who found

$$\rho_t = 94074\{1 + \cdot 0_3 8879\, t + \cdot 0_6 975\, t^2 + \cdot 0_9 20\, t_3\}.$$

The Electrical Conductivities of Dilute Thallium Amalgams.

The conductivity of thallium amalgams has been examined by Bornemann and Rauschenplatt †, and by Pavlovitsch ‡, whilst Feninger § considered the electrical conductivity of dilute amalgams in relation to internal friction. Pavlovitsch examined the electrical conductivity of alloys containing from 0 to 40 per cent. of thallium, and the curve obtained shows a maximum for about 27 per cent. of thallium.

Feninger determined the relative conductivity with respect to mercury of thallium amalgams of the following atomic per cent.:—0·156, 0·308, 0·650 at temperatures 0°, 20°, 40°, 60°, 10°, and 18° C.

Bornemann and Rauschenplatt obtained the following results for the resistivity of dilute thallium amalgams:—

Atomic per cent. of Tl.	Specific Resistance × 10^4.					
	50°	100°	150°	200°	250°	300°
0·98	·9658	1·0112	1·0622	1·1179	1·1820	1·2514
2·85	·9320	·9741	1·0210	1·0700	1·1208	1·1820

In the present experiments the specific resistances of thallium amalgams of concentrations varying from 0·063 gram of thallium in 100 grams of mercury, to 1 per cent. of thallium in mercury, were examined at room temperature and 100° C., and an amalgam of concentration 0·5 gram of thallium per 100 grams of mercury at higher temperatures up to about 300° C.

---

* J. W. Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry,' vol. iv. pp. 729–732. Williams, *loc. cit.*

† Bornemann & Rauschenplatt, *Metallurgie*, ix. p. 510 (1912).

‡ Pavlovitsch, *Russ. Phys. Chem. Soc.* xlvii. p. 29 (1915).

§ Feninger, *loc. cit.*

Owing to the rapid oxidation of the amalgams, the experiments were carried out in a vacuum or in an atmosphere of hydrogen (for high temperatures) in the apparatus previously described (fig. 3). The results are collected in Tables II., III., and IV.

In Table II. the concentration "*c*" is expressed in gram atoms per 100 gram atoms of mercury, *i. e.* in atom atoms per cent. approximately. The tables are self-explanatory.

TABLE II.

Thallium Amalgams.

Temperature t° C.	Percentage weight of thallium in mercury.	Concentration "*c*."	Resistivity of pure mercury at t° C. $\times 10^9$.	Conductivity of mercury at t° C. $\times 10^1$.	Resistivity of amalgam $\times 10^9$.	Conductivity of amalgam at t° C. $\times 10^1$.
13·3°	·0634	·0622	95200	105042	95083	105172
	·1275	·1252	,,	,,	94963	105305
	·2250	·2505	,,	,,	94727	105566
	·3826	·3758	,,	,,	94492	105829
	·5003	·4914	,,	,,	94278	106070
	·7494	·7361	,,	,,	93820	106587
	1·0000	·9823	,,	,,	93375	107095
100°	·0634	·0622	103361	96749	103216	96884
	·1275	·1252	,,	,,	103076	97016
	·2550	·2505	,,	,,	102800	97276
	·3826	·3758	,,	,,	102517	97544
	·5003	·4914	,,	,,	102249	97800
	·7494	·7361	,,	,,	101698	98330
	1·0000	·9823	,,	,,	101159	98854
13·3°	·5003	·4914	95200	105042	94278	106070
100	,,	,,	103361	96749	102249	97800
183	,,	,,	112544	88854	110910	90163
255·5	,,	,,	121797	82104	119788	83481
294·8	,,	,,	127137	78654	124448	80355

Bornemann and Rauschenplatt's results show that the temperature coefficient of resistivity of the amalgams decreases with increase of temperature. This is contrary to the results found in the present experiments. The resistivity of an amalgam of concentration "*c*" = ·98 at 100° found in these experiments is very close to the value given by Bornemann and Rauschenplatt, the values differing by only ·04 per cent.

Curve I.

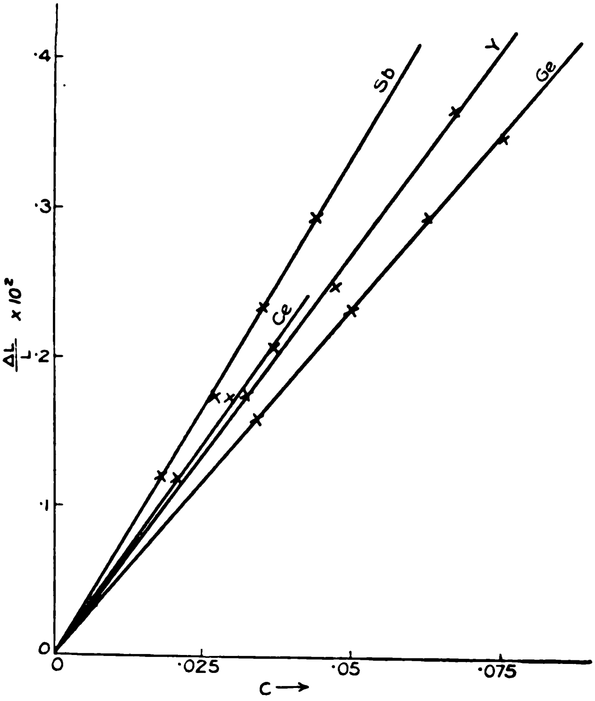


Table III.

Variation of the resistivity of an amalgam of Thallium of concentration "*c*" = ·4914 with temperature.

Temperature t° C.	Resistivity of amalgam at t° C.	Average temperature coefficient of resistivity 13·3 – t° C. for mercury × 10^4.	Average temperature coefficient of resistivity 13·3 – t° C. for amalgam × 10^4.	$\frac{\Delta L}{L} \times 10^2$.
13·3°	94278	……	……	·978
100	102249	9·888	9·752	1·0866
183	110910	10·736	10·396	1·4731
255·5	119788	11·535	11·172	1·6774
294·8	124448	11·917	11·368	2·1633

In Table III. $\frac{\Delta L}{L}$ is the increase of conductivity relative to that of mercury at the same temperature. For the same concentration it increases with temperature.

Table IV. shows the average temperature coefficient of the various amalgams of different concentrations between 13°·3 C. and 100° C. The average temperature coefficient diminishes as the concentration increases.

TABLE IV.

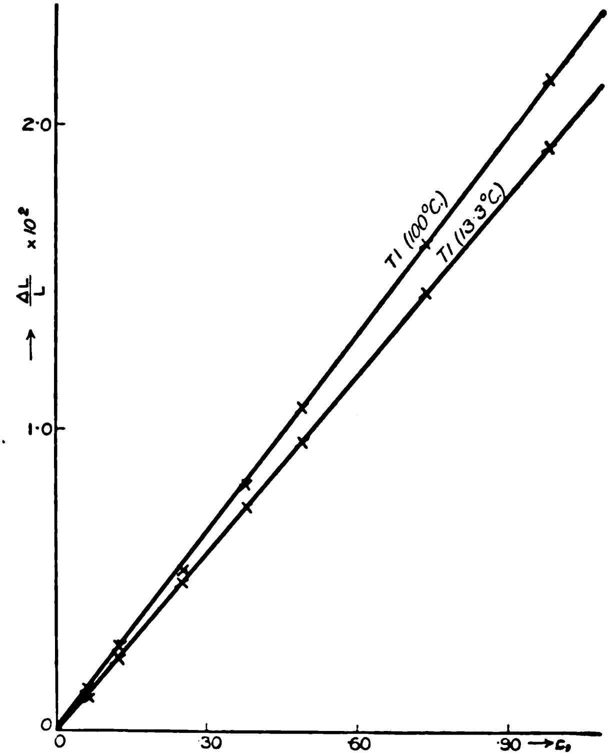
Average temperature coefficient of resistivity of Thallium Amalgam between 13°·3 and 100° C.

Concentration "*c*."	Temperature coefficient of resistivity of amalgam between 13°·3 and 100° C. $\times 10^4$.
·0622	9·866
·1252	9·854
·2505	9·829
·3758	9·796
·4914	9·752
·7361	9·685
·9823	9·615

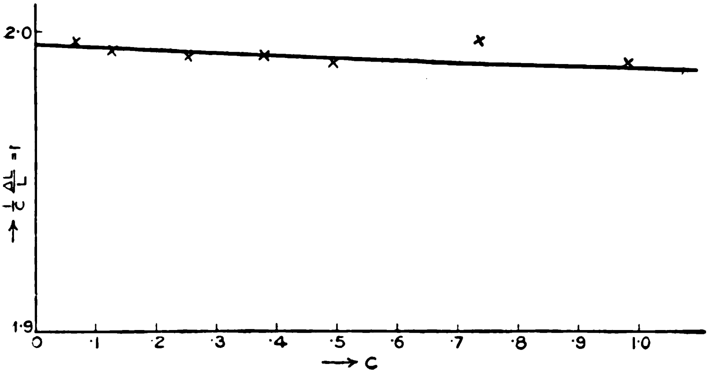
Curve II shows the variation of the relative increase of conductivity $\frac{\Delta L}{L}$ with concentration "*c*" at 13°·3. Since it is a straight line, the increase of conductivity relative to mercury is proportional to the concentration for dilute amalgams of thallium. Curve II also gives the variation of $\frac{\Delta L}{L}$ with "*c*" at 100°.

This again is a straight line, showing that $\frac{\Delta L}{L}$ is proportional to "*c*" at 100° C.

Curve II.



Curve III.



Curve III gives the variation of $\frac{1}{c}\frac{\Delta L}{L}$ with "*c*" at 13°·3, *i. e.*, the variation of the ratio of the increase of conductivity relative to mercury, to the concentration, with the concentration. It is practically a straight line for dilute solutions.

From this curve, the value of l_{∞}, the ratio of the relative increase of conductivity with respect to mercury to the concentration, at infinite dilution, is obtained.

The Electrical Conductivity of Germanium Amalgams.

As far as the author is aware, no previous determination of the conductivity of germanium amalgams has been made, and the measurements are rather difficult, on account of the low solubility of germanium in mercury. It was found necessary to heat the mercury to a temperature of about 250° C. before any appreciable quantity of germanium would pass into solution, and all measurements, with one exception, were carried out at temperatures of about 300° C. The determinations of the resistance of the amalgams were made as in the previous experiments, the quartz tube being used. The amalgams were heated for several hours in the bath at about 300° C. in order to ensure that the metal had diffused through the capillary, and until a constant value of the resistance was obtained.

The mercury in the cup was replaced by a germanium amalgam of the same concentration as that in the capillary tube, so that the leads were always in the same amalgam during the two measurements taken to obtain a value of the resistance. This precaution was taken in all experiments carried out on amalgams. The results are given in Tables V. and VI.

Curve I shows the variation of the relative increase of conductivity, with respect to mercury, with concentration. It is seen that these quantities vary proportionately.

From the results obtained at 250°·1 C. it is seen that the average temperature coefficient of resistivity of the amalgam is slightly less than that of mercury.

Since the amalgams are so extremely dilute, the value of l_{x}, the ratio of the increase of conductivity relative to mercury to the concentration, at infinite dilution, is taken as the mean of the values of $\frac{1}{c}\frac{\Delta L}{L}$ obtained. The values of this quantity for dilute amalgams are not very accurate owing to the small changes in conductivity produced, and errors of from 4 to 10 per cent. are possible on the average.

TABLE V.

Nature of Amalgam.	Temperature $t°$ C.	Percentage weight of substance in mercury.	Concentration "c."	Resistivity of mercury at $t°$ C. $\times 10^{9}$.	Conductivity of mercury at $t°$ C. $\times 10^{1}$.	Resistivity of amalgam at $t°$ C. $\times 10^{9}$.	Conductivity of amalgam at $t°$ C. $\times 10^{1}$.
Germanium	301·8°	·01227	·03392	128140	78040	127933	78166
	,,	·01824	·05042	,,	,,	127838	78224
	,,	·02283	·06310	,,	,,	127762	78271
	,,	·02724	·07529	,,	,,	127691	78314
	250·1°	·01824	·05042	120988	82652	120729	82830
Antimony	301·8°	·01096	·01827	128140	78040	127984	78135
	,,	·01617	·02696	,,	,,	127915	78177
	,,	·02107	·03513	,,	,,	127838	78224
	,,	·02650	·04418	,,	,,	127761	78271
Yttrium	302°	·01450	·03272	128169	78022	127943	78160
	,,	·02120	·04784	,,	,,	127849	78217
	,,	·03000	·06770	,,	,,	127701	78308
	,,	·04220	·09523	,,	,,	127494	78435
Cerium	300°	·01440	·02058	127876	78201	127720	78296
	,,	·02090	·02986	,,	,,	127655	78336
	,,	·02500	·03572	,,	,,	127611	78363
Aluminium	300°	·01000	·07395	127876	78201	127405	78490
	,,	·01953	·14442	,,	,,	126992	78745

TABLE VI.

Nature of Amalgam.	Temperature t° C.	Concentration "c."	$\frac{\Delta L}{L} \times 10^2$.	$\frac{1}{c}\frac{\Delta L}{L} \times 10^2$.	$l_\infty \times 10^2$.
Thallium	13·3°	·06220	·1243	1·997	1·995
	"	·1252	·2497	1·994	
	"	·2505	·4991	1·992	
	"	·3758	·7488	1·993	
	"	·4914	·9780	1·990	
	"	·7361	1·4710	1·998	
	"	·9823	1·9543	1·990	
	100°	·0622	·1394	2·241	2·208
	"	·1252	·2760	2·205	
	"	·2505	·5450	2·176	
	"	·3758	·8220	2·187	
	"	·4914	1·0866	2·211	
	"	·7361	1·6340	2·220	
	"	·9823	2·1761	2·215	
	13·3°	·4914	·9780	1·990	
	100·0	"	1·0866	2·211	
	183·0	"	1·4731	2·998	
	255·5	"	1·6774	3·414	
	294·8	"	2·1633	4·402	
Germanium ...	301·8°	·03392	·1618	4·770	4·7
	"	·05042	·2359	4·679	
	"	·06310	·2964	4·697	
	"	·07529	·3505	4·655	
	250·1°	·05042	·2155	4·274	
Antimony	301·8°	·01827	·1213	6·639	6·6
	"	·02696	·1751	6·495	
	"	·03513	·2359	6·715	
	"	·04418	·2966	6·713	
Yttrium	302·0°	·03272	·1765	5·394	5·4
	"	·04784	·2501	5·228	
	"	·06770	·3668	5·418	
	"	·09523	·5291	5·556	
Cerium	300·0°	·02058	·1210	5·88	5·8
	"	·02986	·1730	5·79	
	"	·03572	·2070	5·79	
Aluminium ...	300·0°	·07395	·3702	5·01	5·0
	"	·14442	·6952	4·81	

The Electrical Conductivity of Antimony Amalgams.

The experiments on antimony amalgams were carried out in the quartz tube, as the metal amalgam does not oxidize appreciably. Owing to the low solubility of antimony in mercury, only very dilute amalgams of concentration ·018 to ·044 were used and their resistances found at about 300°, as the mercury had to be heated up to about this temperature before the metal would dissolve.

The results for the four amalgams are given in Tables V. and VI. The relation between $\frac{\Delta L}{L}$ and "*c*" at 301°·8 is shown graphically in Curve I. It was found that the relative increase of conductivity with respect to mercury is proportional to the concentration "*c*."

As in the case for all other amalgams, the mercury was heated at about 300° C. for several hours in order to obtain reliable values of the resistances. The value of l_∞ is taken as the mean of the value of $\frac{1}{c}\frac{\Delta L}{L}$, since the amalgams approach infinite dilution.

Yttrium Amalgams.

The electrical resistances of the four yttrium amalgams were found at 302°, using the quartz tube. The same precautions as with the previous amalgams were taken. The amalgams were of concentrations ranging from ·03 to ·09.

The results are shown in Tables V. and VI., and graphically in Curve I.

Since the curve is a straight line, the increase of conductivity relative to mercury is proportional to the concentration.

The value of the ratio of the increase of conductivity relative to mercury, to the concentration for infinite dilution is taken as the mean of the values of $\frac{1}{c}\frac{\Delta L}{L}$, since the amalgams are so dilute.

Cerium Amalgams.

Owing to the oxidation of cerium, when in amalgam, the experiments were carried out in the tube previously described (fig. 3).

The tube was evacuated and filled with pure dry hydrogen to a pressure which increased to one atmosphere at the temperature at which the determinations of resistance were made. Since the solubility of cerium in mercury is very low, three amalgams of concentration between ·02 and ·04 were used at 300°.

Tables V. and VI. show the results obtained, and Curve I gives the variation of $\frac{\Delta L}{L}$ with "*c*."

The value of $\frac{1}{c}\frac{\Delta L}{L}$ at infinite dilution is taken as the mean of the values obtained for the respective concentrations, as the amalgams were extremely dilute.

Aluminium Amalgams.

A few preliminary experiments were carried out on the conductivity of dilute aluminium amalgams.

Owing to the rapid oxidation of the amalgam in air, the experiments were carried out in an atmosphere of hydrogen. Two amalgams of concentrations 0·0739 and 0·1444 were employed, and the results are given in Tables V. and VI.

The relative increase of conductivity with respect to mercury is approximately proportional to the concentration.

Beryllium Amalgams.

L. F. Nilson and O. Petterson [*] prepared a beryllium amalgam by the electrolysis of a concentrated solution of beryllium chloride with a mercury cathode. According to W. Ramsay [†], the amalgam so prepared is very dilute, since more concentrated amalgams are readily attacked by the electrolyte, and it is readily oxidized in air. An attempt was made to prepare a dilute beryllium amalgam in an atmosphere of hydrogen, and measure its conductivity at about 300° C. About 0·004 gram of beryllium was added to 200 grams of mercury in the sealed apparatus containing hydrogen described previously. The apparatus was kept at a temperature of about 300° C. for several hours, but no change of resistance due to solution of the beryllium in the mercury could be detected. As a change of resistance of one part in eight thousand could be detected by means of the apparatus employed, it was concluded that either beryllium did not enter into solution even at 300° C., or that the amalgam produced was so dilute that its effect on the conductivity was negligible.

Discussion of Results.

For purposes of discussion the Table VI. has been constructed for the results obtained for all the amalgams. The concentration "*c*" is expressed in gram atoms of the metal per 100 gram atoms of mercury, *i. e.*, approximately in atom atoms per cent.

---

[*] *Ber.* xi. p. 381 (1878).

[†] Journ. Chem. Soc. lv. p. 530 (1889).

$\frac{\Delta L}{L}$ is the increase in conductivity relative to that of mercury at the same temperature.

The fifth column gives the ratio of $\frac{\Delta L}{L}$ to "c," i.e., the values of "l."

The sixth column gives the value of "l" for infinite dilution, *i.e.*, the value of the ratio of the increase of conductivity relative to mercury at the same temperature to the concentration, when the latter is very small.

According to Skaupy's theory, which was discussed in the introduction to this paper, the value of $H_\infty = l_\infty + r_\infty$ should be of the same order of magnitude for the different metals dissolved in mercury. Unfortunately, the author has not at his disposal values of r_∞ for the different amalgams, whose conductivities have been measured, and is consequently obliged to consider the values of l_∞ in relation to the different amalgams. From the values given in Table VI. the conclusion can be drawn that the value of l_∞ is of the same order of magnitude for all the amalgams examined. The values for germanium, yttrium, cerium, and antimony vary from $4{\cdot}7 \times 10^{-2}$ to $6{\cdot}6 \times 10^{-2}$ but the value for thallium is decidedly low, $1{\cdot}995 \times 10^{-2}$ when taken at a temperature of about 13°·3 C.

It is of interest, however, to point out that the value of $\frac{1}{c}\frac{\Delta L}{L}$ for thallium amalgams increases rapidly with temperature, its value changing from $1{\cdot}995 \times 10^{-2}$ at 13°·3 C. to $4{\cdot}40 \times 10^{-2}$ at 294°·8 C. If the latter value is taken for l_∞, it compares reasonably well with the values obtained for the other amalgams at practically the same temperature.

In the present investigation the conductivity of dilute amalgams of the various metals was examined, and there is very little change in the value of "l" with change of concentration. Consequently, there is not much point in discussing the values of $\frac{l_\infty - l}{c}$.

SUMMARY.

1. The resistivity and conductivity of mercury have been measured in a quartz tube at temperatures varying from 0° to 300° C. The specific resistance at any temperature "t" within this range is given by the formula :

$$\rho_t = \rho_0(1 + {\cdot}0_3\,8877t + {\cdot}0_6\,977t^2 + {\cdot}0_9\,19t^3).$$

2. The resistivity and conductivity of dilute amalgams

of thallium, germanium, antimony, yttrium, cerium, and aluminium have been measured. The conductivities of germanium, antimony, yttrium, and cerium amalgams were measured at about 300° C., and the conductivities of amalgams of thallium of various concentrations were determined at 13°·3 C. and 100° C. In the case of thallium amalgams of concentration ·49, the measurements were extended to 300° C. It was found impossible to prepare an amalgam of beryllium of sufficient strength to measure its conductivity.

3. It was found that the relative change of conductivity with respect to mercury at the same temperature is proportional to the concentration for the dilute amalgams employed in these experiments, and that the temperature coefficient of increase of resistance in the case of thallium amalgams decreases with increase of concentration.

4. The results were examined in relation to a theory put forward by Skaupy, and it was found that the value of l_∞, *i. e.*, the value of $\frac{1}{c}\frac{\Delta L}{L}$ at infinite dilution, was of the *same order of magnitude* for the amalgams examined. The meaning of this result is that atom for atom the effect of the different metals on the conductivity of mercury is about the same.

The experiments described above were carried out in the Physical Laboratories of the University College of Swansea. In conclusion, I wish to thank Professor E. J. Evans for his valuable suggestions and guidance during the course of the research.

December 1925.

II. *The Magnetic Susceptibilities of some Alkalis.* By W. Sucksmith, *B.Sc., Lecturer in Physics, University of Bristol* [*].

THE experiments described in the present paper are an account of measurements on the susceptibilities of the alkalis over a range of temperatures in the solid and liquid states. The original intention was to try to extend these also to the gaseous state. It has been shown that sodium and potassium [†] are monatomic in the gaseous state, and for this reason a knowledge of their susceptibility is desirable as a basis to modern magneton theory. Unfortunately, the difficulty of finding a suitable container above 500° C. proved prohibitive. However, the results obtained in the solid and liquid states are not without interest, and the following is an account of measurements made up to the neighbourhood of 500° C.

---

[*] Communicated by the Author.

[†] Dewar & Scott, Proc. Roy. Soc. A, xxix. p. 490.

The method employed is essentially that of Faraday, in which the force exerted on a small quantity of the substance in a non-uniform magnetic field is measured. The force on an element of mass dm in the direction x is

$$dF = \chi dm H \frac{\partial H}{\partial x},$$

where X is the susceptibility per unit mass, H the magnetic field whose gradient in the direction of the force, *i.e.*, perpendicular to H, is $\frac{\partial H}{\partial x}$. If the volume is limited to one in which the variation of $H\frac{\partial H}{\partial x}$ over the volume occupied by the total mass m is negligible, we can write

$$F = \chi m H \frac{\partial H}{\partial x}.$$

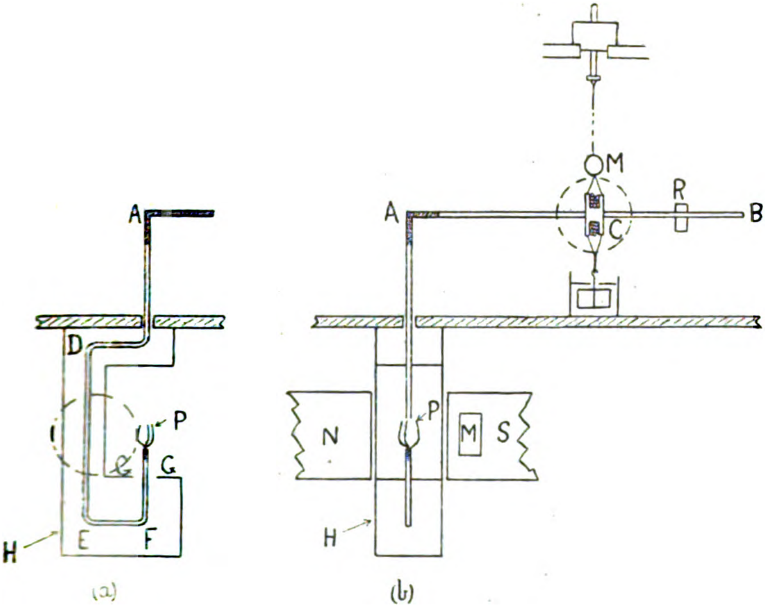
The point at which the substance is placed is that at which $H\frac{\partial H}{\partial x}$ is a maximum, and consequently the error due to accidental displacement is a minimum.

As a non-uniform field is difficult to measure with accuracy, a comparison method was used, the standard adopted being water, whose susceptibility is known accurately.

The force F is neutralized electro-magnetically, and the substance brought back to its original position. In this way, all measurements are made in the position of maximum sensitivity and least error.

The general disposition of the apparatus is shown in fig. 1, (*a*) looking along the direction of, and (*b*) perpendicular, to the direction of the magnetic field. The torsion arm ACB is of thin-walled glass-tubing, supported at C by a suspension of phosphor-bronze strip. The upper end of the strip is attached to a torsion head which carries a three-dimensional adjustment. The length of the suspension is about 7 cm., as it was found that, other things being equal, a short suspension was less affected by extraneous disturbances than a larger one. An L-shaped piece of copper rod is fixed into A, by means of which the arm ADEF carrying the specimen is attached. This suspension rod is also of thin glass tubing, external diameter 2·5 mm., and carries a platinum fork which holds the phial containing the alkali. The point F is vertically under A, so that no sideways displacement of the system is possible when the phial is placed in the fork.

Fig. 1.



(a) (b)

The rider R is used to preserve balance of the torsion arm when different masses are used. To prevent disturbances due to convection currents, a brass box can be placed over the apparatus, whilst on the under side of the table, the arm ADEF is enclosed in the brass case H. The furnace is placed in the position GG.

The inner wall of the furnace consists of a copper tube, closed at one end with a copper plate. This ensures equilibrium of temperature over the specimen. On this copper tube is wound the heating coil of constantan, insulated from it by means of asbestos paper and embedded in a cement composed of water glass and china clay. The whole is enclosed in a double-walled brass case, so as to allow water cooling. It was found further, that about an inch of water in the brass case H below EF greatly improved the steadiness of the zero at higher temperatures.

The temperature of the furnace was measured by a platinum to platinum-rhodium thermocouple attached to its inner wall, the junction being as close as possible to the position occupied by the phial.

At C is the neutralizing coil which is situated midway between two fixed Helmholtz coils (indicated by a dotted circle in fig. 1 *b*), the turns being at right angles to those of the moving coil. The current is passed through the coil by means of long spiral leads of 48 S.W.G. copper. These leads are not sufficient to affect the torsion constant appreciably, and, furthermore, any such effect merely alters the sensitivity slightly. To the lower end of the coil C is fixed a damping vane immersed in a mixture of lubricating oil and paraffin of such consistency as to make the system dead-beat.

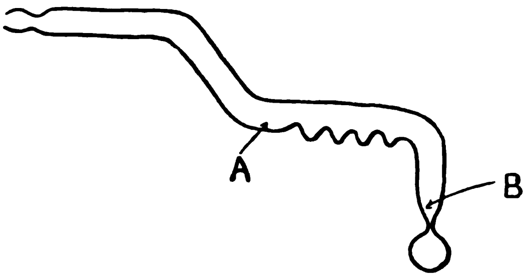
The Helmholtz coils and the moving coil are in series with a mirror dynamometer of low impedance, through which alternating current can be passed to neutralize the displacement due to the magnetic forces. The deflexion of the dynamometer is noted and the mean direct current producing the same deflexion is measured on a standard milliammeter. The square of this current is proportional to the magnetic force on the phial and its contents.

Alternating current is necessary owing to the large stray field of the electromagnet in which the coil C moves. The source of this A.C. was a motor alternator run off a direct current battery. This is essential in order to keep the voltage quite steady. The frequency was about 40 cycles, whilst that of the A.C. used for heating the furnace was 93, so that no interaction can occur. The current is cut down to a suitable value by non-inductive resistances, which are sufficient to swamp the inductive lag in the dynamometer and coils.

The substances dealt with must as far as possible be free from ferromagnetic impurity. Further, special precautions must be taken to prevent oxidation of the metal before it is sealed into its container. Various materials were tried for use as container, and, finally, "Pyrex" glass was found most suitable. The alkalis, even Cs, have little action on this material over the range of temperature employed, and the evacuated thin-walled phials used only begin to soften at about 550° C.

The metal was originally contained in evacuated glass tubes, which were broken under water-free naphtha. About 1 gm. of the substance was cut off and quickly dried on filter paper and introduced into a "Pyrex" tube of the shape shown in fig. 2. (The diameter of the tube and phial was about 1·2 cm.) This was immediately connected with pressure tubing to an evacuated reservoir and high vacuum pump, which reduced the pressure immediately to 1 or 2 cm. The pump lowered this to 0·1 mm. in a few minutes, so that oxidation was kept small. As soon as the minimum pressure was reached, the metal at A (fig. 2) was gently heated until melted, and kept at 200° to 300° C. for about half an hour until the absorbed gas was released and pumped off. During this procedure, the small quantity of naphtha which had adhered to the metal was deposited on the walls of the tube as a black scale, or left behind on the corrugations of the tube when it was tilted to run the metal into space B above the phial. Successive heating and cooling resulted in drawing the required quantity into the phial. After a final heating, the phial was sealed and melted off at the constriction, the resulting projection being heated to redness and then depressed with a carbon rod, so as to make the phial as near spherical as possible.

Fig. 2.



The electromagnet used was of the Du Bois type. In order to obtain a large enough space for the introduction of the furnace, the pole pieces, 8 cm. diameter, were fixed at about 5 cm. apart. The faces of the pole pieces, NS in fig. 1*b*, are inclined at 10° to each other, so that the position at which $H\frac{\partial H}{\partial x}$ is a maximum is about 5 cm. outside the line joining their centres. The centre of the phial was placed at this point in all determinations, adjustments being made by means of a travelling microscope. The position midway between the two pole faces was adjusted by viewing the phial directly, and the position perpendicular to the lines of force by means of reflexion at a plane mirror M attached to the pole piece S inclined at about 45° to the line of sight.

Let ι_1 be the mean neutralization current for the substance and phial,
ι be that for the phial alone,
ι_2 be that for the phial and water occupying the same volume as the substance originally occupied, and χ_a, χ_w and χ the specific susceptibilities of air, water, and substance, respectively. If the phial be placed in the same position for each determination, then

$$K(\iota_1^2-\iota^2) = (\chi M - \chi_a m_a) H \frac{\partial H}{\partial x},$$

$$K(\iota_2^2-\iota^2) = (\chi_w m_w - \chi_a m_b) H \frac{\partial H}{\partial x}.$$

In these equations K is a numerical constant, m_a the mass of air occupying the internal volume of the phial, M the mass of substance in the phial, and m_b the mass of air occupying the same volume as the water. From this it is seen that

$$\chi = \frac{1}{M}\left\{\chi_a m_a + (\chi_w m_w - \chi_a m_b)\frac{\iota_1^2-\iota^2}{\iota_2^2-\iota^2}\right\}.$$

The specific susceptibilities of water and air are taken as $-0{\cdot}72\times10^{-6}$ and $+23{\cdot}8\times10^{-6}$, respectively, at 20° C.

At ordinary temperatures measurements were taken at fields corresponding to 4, 6, 8, 10, and 12 amperes, whilst with varying temperatures the field used was that due to 10 amperes. The constancy of susceptibility with different fields shows the absence of ferromagnetic impurity. The Na and K contained no detectable trace of iron. In the case of Rb and Cs, slight quantities were present, presumably due to the method of preparation, which is usually that of electrolysis using an iron electrode. The lithium used (Kahlbaum) contained so much iron as to make measurements impossible. In the case of Cs and Rb measurements at different fields were taken at various temperatures throughout the range in order to eliminate the effect of ferromagnetic impurity by the method due to Owen *. This takes advantage of the fact that for high values of the magnetizing

---

* Owen, *Ann. der Phys.* xxxvii. p. 657 (1912).

field, whilst the susceptibility of para- and dia-magnetic substances is independent of the field, that of ferromagnetic substances varies inversely as the field.

In taking measurements at different temperatures, the intervals in the neighbourhood were about 5° C. around the melting-point and 20°–50° over the liquid state. Sufficient time was allowed to elapse between measurements to allow the substance and phial to come to temperature equilibrium.

After a series of measurements had been made, the substance had to be removed from the phial to allow the susceptibility of the latter to be measured over the same range. To do this, two narrow cuts were filed through the neck of the phial, after which it was placed in methylated spirit (containing 5 to 10 per cent. water) to remove the alkali. This method was successful for Na and K, but far too vigorous for removing Cs and Rb, owing to their great affinity for water. For these substances, the phial was cut as before and placed in an evacuated tube. The majority of the metal was distilled off, and the small residue removed with alcohol. The amount of glass filed off was less than 1 per cent. of the total weight of the phial, which has a small diamagnetic susceptibility, so that the error involved is negligible.

The results for Na, K, Rb, and Cs are shown in fig. 3, the curves representing the means of 6, 4, 2, and 2 results respectively, the mass susceptibility decreasing with increasing atomic number. Honda[*] and Owen[†] have experimented on these substances and found that their susceptibilities remain constant over a range of temperature from −170° to +10° C. There is no satisfactory theory explaining the fact that a large number of elements exhibit a paramagnetic susceptibility independent of temperature. It seems probable that with these elements the decrease with increasing atomic number is due to the increasing diamagnetic contribution of the L, M, and N rings, on which is superposed a paramagnetic effect presumably due to the additional electron.

There is gradual change in susceptibility up to the melting-point for each of the substances, followed by a sudden change when fusion takes place. These changes may be explained in the light of the following evidence.

Oxley[‡] has shown that the usual order of change of susceptibility (about 5 per cent.) on crystallization demands the existence of a local molecular field of 10^7 gauss. This leads to an estimate of the potential energy, associated with the crystalline state as a result of the molecular grouping equal to $\frac{1}{2}H_cI$ ergs per unit volume, where H_c is the molecular

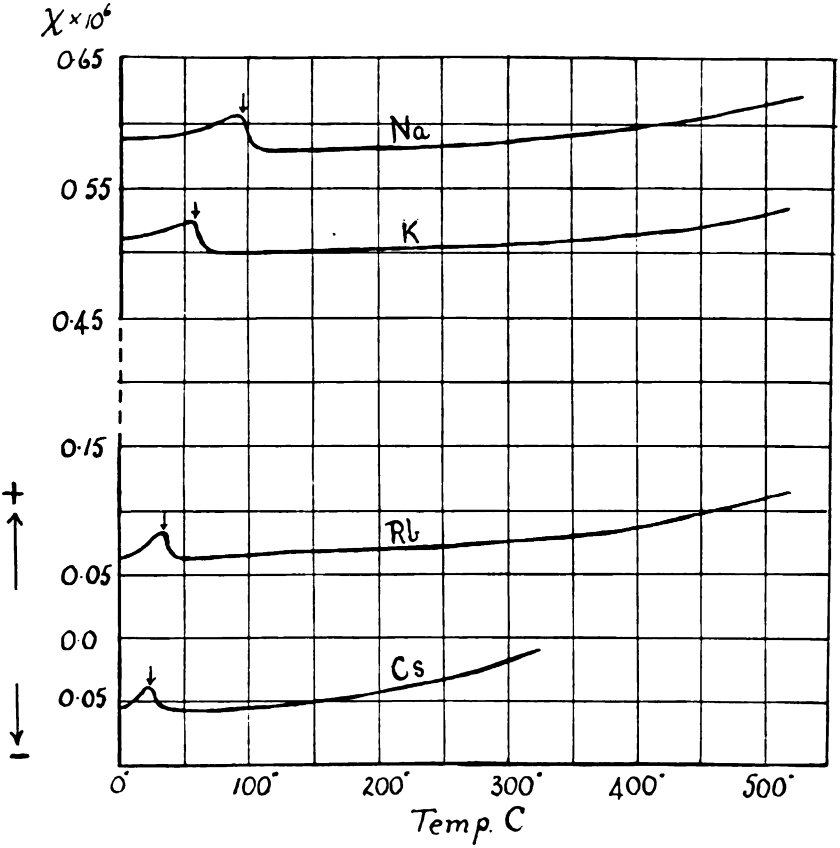
---

[*] Honda, *Ann. d. Phys.* xxxii. p. 1027 (1910).

[†] Owen, *loc. cit.*

[‡] Oxley, Phil. Trans. Roy. Soc. A, ccxiv. p. 109 (1914).

Fig. 3.



field, and I the local intensity of magnetization per unit volume. The thermal equivalent of this will in general represent the latent heat of fusion, but a small fraction of the energy may be dissipated before fusion is reached. This would add to the normal variation of specific heat with temperature an additional positive term. It appears that this is actually the case with sodium. Griffiths * has shown that this metal shows an abnormal rise of specific heat up to the melting-point, followed by a subsequent decrease after fusion has taken place. Further evidence to support this view lies in the fact that sodium † and potassium ‡ both give well-defined X-ray diffraction patterns at the temperature of liquid air, whilst at ordinary temperatures they give no effect. Increase of temperature has evidently broken up the crystal lattice before fusion takes place. These facts seem to support the view that the shape of the susceptibility curves around the melting-point is due to the breaking up of molecular aggregates.

The gradual increase after fusion leads one to look for the cause as being due to the presence of alkali vapour in the space above the liquid. This was negatived by measurements on a phial of 2 c.c. capacity containing about one-tenth that volume of sodium, whereas the vacuous space was usually about 0·3 c.c. in a phial of 1·5 c.c. capacity.

The specific susceptibilities are $+0{\cdot}62$, $+0{\cdot}53$, $+0{\cdot}11\times 10^{-6}$ for Na, K, and Rb respectively at 500° C. and $-0{\cdot}02\times 10^{-6}$ at 300°. for Cs. It is interesting to compare these values with those which would be given by allotting one Bohr magneton to each of these substances in the vapour state. At the boiling-points these would be 14·2, 9·2, 4·2, and $3{\cdot}0\times 10^{-6}$ respectively. If this is to hold, very great increases of susceptibility in the range between 500° C. and the boiling-points must take place.

In conclusion, the writer wishes to express his indebtedness to the Colston Research Society of the University of Bristol for a grant towards expenses, and to Prof. A. M. Tyndall for his interest during the progress of the work.

---

[*] E. Griffiths, Proc. Roy. Soc. A, lxxxix. p. 561 (1914).

[†] Hull, Phys. Rev. (2) x. p. 661 (1917).

[‡] McKeehan, Proc. Nat. Acad. Sci. viii. p. 254 (1922).

III. *Determination of the Size and Weight of Single Submicroscopic Spheres of the Order of Magnitude* $r=4.10^{-5}$ *cm. to* 5.10^{-6} *cm., as well as the Production of Real Images of Submicroscopic Particles by means of Ultraviolet Light.*

By FELIX EHRENHAFT, *Dr.Phil., Acting Professor of Physics and Head of Physics Institute III. of the University of Vienna, and* EMANUEL WASSER, *Dr.Phil., of Vienna* *.

[Plate I.]

§ 1. *Introduction.*

AS is well known, it is possible to hold single electrically charged colloidal test bodies between the plates of a horizontal condenser, to illuminate the space between the plates with a microscope objective, and to make observations with a microscope adjusted perpendicular to the direction of illumination against a dark background. This procedure was devised by Ehrenhaft †, and has recently been described anew in the Philosophical Magazine ‡. The smaller the diameter of the condenser plates (9 mm. to 2 mm.), the greater may be the aperture of the microscope objective applied in this procedure.

§ 2. *Method of Weight Determination.*

The problem of the determination of the magnitude of submicroscopic bodies appears to have become of great importance for many problems of modern physics. The methods of the determination of magnitude can be free from objection only under the condition that they be carried out independently of other important physical effects of the same order of magnitude §. They must, for example, be independent of the assumption of the existence or non-existence of an elementary quantum of electricity, as well as of the question as to divisibility or indivisibility and equality of charge on the various test bodies. In this way there arose the idea * of determining in a purely mechanical way a law of resistance for small spheres moving in a gas by means of velocity measurements carried out on the same test bodies at different gas pressures. Up to the present time this was successful only for test bodies of magnitudes down to $3{\cdot}5 . 10^{-5}$ cm. The critical and interesting colloidal order of magnitudes begins just at this point.

---

* Communicated by the Authors.

† F. Ehrenhaft, *Anz. d. Wien. Akad. d. Wiss.* no. vii. March 4, 1909; no. x. April 21, 1910; no. xiii. May 12, 1910.

‡ F. Ehrenhaft, Phil. Mag. vol. xlix. April 1925, p. 633.

§ F. Ehrenhaft, *Phys. Zeits.* xii. p. 102 (1911); Discussion at the "Deutscher Naturforschertag in Jena," R. Bär, *Phys. Zeits.* xxii. p. 617 (1921).

Two circumstances have prevented the setting up empirically of a law of resistance for this order of magnitude. First may be mentioned the difficulty in the selection of a suitable material for experiment. A fluid would appear to come at first into consideration. All fluids however, with the exception of mercury, are exceptionally transparent, so that it would be difficult to render them visible against a dark background when in this state of fine division. In the second place, fluids evaporate. Further, the uniform velocity of fall of these fluid droplets in a resisting medium (gas) is, on account of their small density, so small that the experiments would seem to have little hope of success, for the vertical component of the Brownian movement would in this case be a disturbing factor. We are hence limited for the first to mercury. The mercury droplets produced by evaporation, pulverization, etc. have a very great reflecting power and a sufficiently great velocity of fall. The second

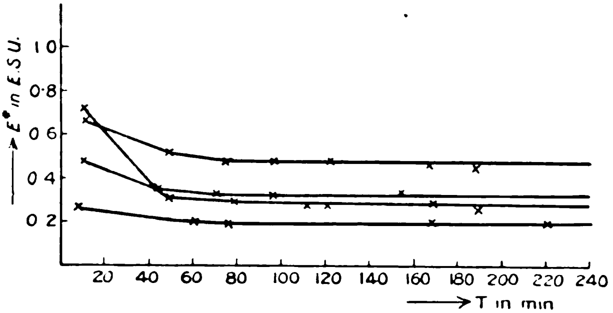
---

* It was M. Reinganum who first pointed out that it would be possible to reach a decision concerning the law of resistance by making observations on the same test body at different pressures (M. Reinganum, *Verh. d. Deutsch. phys. Ges.* xii. p. 1025, 1910). E. Meyer and W. Gerlach then observed the same test body at different gas pressures in a condenser of the same dimensions as Millikan's (E. Meyer and W. Gerlach, *Ann. d. Phys.* xlvii. p. 244, 1915). Following this, I. Parankiewicz observed the same selenium sphere at several pressures in an Ehrenhaft condenser and demonstrated the validity in these test bodies of Cunningham's correction to Stokes's law (I. Parankiewicz, *Phys. Zeits.* xix. p. 280, 1918). In the discussion at the Physikertag in Jena about the hypothesis of small densities (Bär), F. Ehrenhaft referred anew to the experimental determination of the law of resistance, demanded by him in 1911, and suggested gold in inert gases as suitable material for experiment (*loc. cit.*). Th. Sexl recently computed the Cunningham correction factor from the observations of Millikan and Derieux on a non-evaporating mercury drop and found it to be 0·86 (Th. Sexl, *Z. f. Phys.* xxvi. p. 371, 1924). Finally J. Mattauch, experimenting in our institute with sprayed oil, proved in a purely mechanical way the validity of the law of resistance, which agrees with that of Millikan. He did it by varying the pressure around differently sized oil-drops of microscopic order of magnitude and did not make use of the assumption, used by Millikan, of the equality of the charges on different drops (existence of an elementary quantum) (J. Mattauch, *Z. f. Phys.* xxxii. p. 439, 1925).

condition, the constancy of mass, has however not yet been clarified for these test bodies.

This difficulty may be removed by a clever artifice. It was found out that in the case of one of the heaviest fluids of low vapour pressure, the so-called Thoulet's solution *, all droplets at first somewhat evaporated on reduction of the pressure around them to 200 mm. mercury. From this state of saturation, which was reached in about 40 minutes, the droplets remained constant for the duration of the observation (2 to 3 hours). The test bodies retained the mass assumed at the first reduction of pressure, also when the pressure about them was increased to atmospheric pressure. The following figure illustrates the evaporation and shows clearly the behaviour of the bodies described above. The time of observation is recorded as abscissa, a magnitude directly proportional to the mass as ordinate †. The extreme points refer to the corresponding second atmospheric pressure.

Fig. 1.



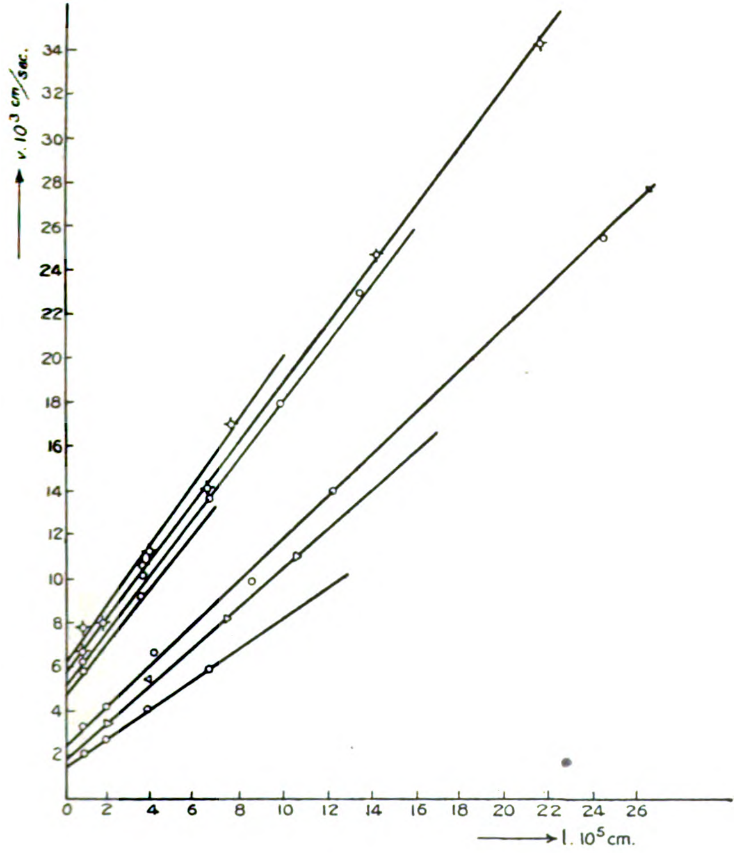
If we now measure the velocity of fall of the same test body at different pressures, returning the body after each measurement to its original position by means of the electrical field, we obtain an empirical relation between the velocities of fall and the corresponding gas pressures. In fig. 2 the mean free path of the molecules, *l*, which is inversely proportional to the pressure, is plotted as abscissa, the velocity of fall as ordinate. The figure shows that the velocity of fall increases with decreasing pressure. It moreover proves that the droplets are of various sizes, but

* The potassium-mercury-iodide ($K_4Hg_2I_4$) was sprayed in dry air. A nearly saturated solution of the density 3·012 was produced.

† This magnitude, the so-called balancing potential E*, is equal to $\frac{mg}{e}$ *i. e.* weight divided by the charge of the test body.

of the same density. If this were not the case, the curves (straight lines) would intersect. The straight lines, however, which represent the dependence of the velocity of fall upon the pressure, form a family of curves with parameter

Fig. 2.



equal to the radius a. If we now form the function $\frac{v}{v_0}=f\left(\frac{l}{a}\right)$ (v_0=intercept in fig. 2), all points of this diagram fall upon a single curve, which is shown in fig. 3. In this way we have completed the proof that all test bodies have a uniform density and that the measurements can be represented by a unitary law of resistance[*].

§ 3. *Method of Computation.*

I. *Linear law of resistance.*—It has frequently been proved[†] that the velocity of small spheres in a resisting medium is proportional to the force acting:

$$v = \mathrm{B}\,.\,\mathrm{P}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the determination of the proportionality constant B we may resort to the theory of hydrodynamics. By means of Stokes's law we may substitute for B the expression

$$\mathrm{B} = \frac{1}{6\pi\mu a}\cdot f\left(\frac{l}{a}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)\ddagger$$

with the condition that the function $f\left(\frac{l}{a}\right)$ should become equal to 1 for infinitely small values of $\frac{l}{a}$, and thus gives the Stokes's law valid for fluids. It may be observed from fig. 2, that the dependence upon pressure is approximately a linear one. According to this we may next assume the function to be linear of the form:

$$f\left(\frac{l}{a}\right) = 1 + \mathrm{A}\frac{l}{a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From this together with (1) and (2), there results the corrected Stokes's law theoretically computed by Cunningham[§]. We then obtain:

$$v = mg\,.\,\mathrm{B}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1\,a)$$

---

[*] The calculation procedure is here necessarily the same as that of J. Mattauch's cited paper on oil-drops of the magnitudes 3·5 to 11 . 10^{-5} cm.

[†] F. Ehrenhaft, *Ann. d. Phys.* lxiii. p. 782 (1920). Yu chen Yang, *Ann. d. Phys.* lxxvi. p. 333 (1925).

[‡] The symbols used in the following formulæ mean respectively: B the mobility, *i. e.* the speed attained by the body under unit force; "a" the radius of the body; μ the coefficient of friction of the medium; σ the density of the test body; mg the weight, *i. e.* the product of the mass of the test body "m" and of the gravitational constant "g."

[§] E. Cunningham, Proc. Roy. Soc. (A), lxxxiii. p. 357 (1910).

or according to (2):

$$v = \frac{1}{6\pi\mu a} \cdot \frac{4}{3}\pi a^3 \sigma g \cdot f\left(\frac{l}{a}\right), \quad . \quad . \quad . \quad (2\,a)$$

and finally, taking account of (3):

$$v = \frac{2}{9} \cdot \frac{\sigma g}{\mu} \cdot a^2 \cdot \left(1 + \mathrm{A}\frac{l}{a}\right). \quad . \quad . \quad . \quad . \quad (4)$$

This can also be written in the form

$$v = v_0 + \beta l, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $v_0 = \frac{2}{9} \cdot \frac{\sigma g}{\mu} \cdot a^2$ and $\beta = \frac{2}{9} \cdot \frac{\sigma g}{\mu} \mathrm{A} a$ [*].

From this we determine for each separate drop the intercept v_0 and the slope β by means of the method of least squares. For each drop there are as many equations as points which lie upon the line. The density assumed known, the expression for v_0 gives us the radius of the test body, the expression for β the constant A of the law of resistance.

TABLE I.

Test body No.	$v \cdot 10^3 \frac{\text{cm.}}{\text{sec.}}$	$v_0 \cdot 10^3 \frac{\text{cm.}}{\text{sec.}}$	β.	$a \cdot 10^5$ cm.	A.	n [†].
27	2·032	1·338	68·72	1·924	0·99	4
32	3·012	2·108	94·80	2·418	1·08	6
46	3·277	1·665	88·83	2·149	1·14	4
45	5·756	4·561	126·38	3·557	0·98	2
44	5·972	4·870	134·36	3·676	1·01	5
29	6·398	5·533	122·95	3·918	0·87	6
25	7·777	6·180	136·48	4·141	0·91	3

[†] n is the number of points for each line in the graph 2.

Table I. gives the corresponding values. The constants A, which we separately determined for each test body, lie all in the interval 0·9 to 1·1, and hence, with comparatively small deviations, within the theoretical limits. The assumption seems, therefore, plausible that a common law of resistance exists for all test bodies. This is shown by fig. 3. In this figure all points of the graph 2 have been brought upon a common curve by means of the relation

---

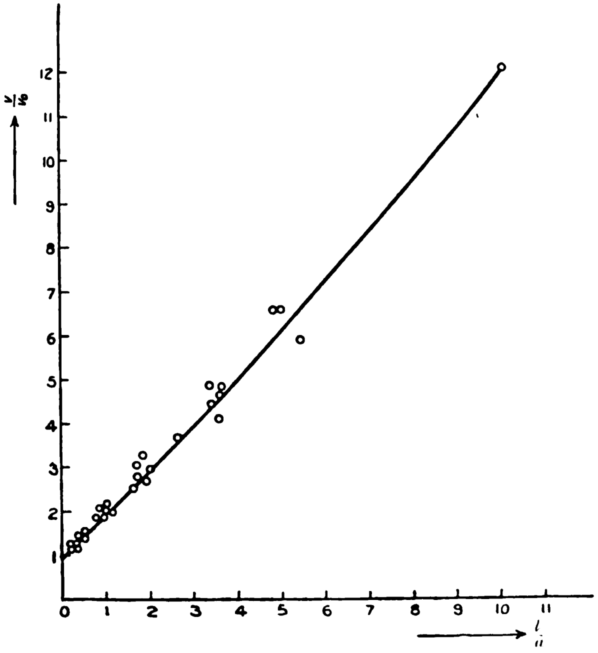
[*] *Cf.* R. Bär and F. Luchsinger, *Phys. Zeits.* xxii. p. 225 (1921).

$$\frac{v}{v_0}=f\left(\frac{l}{a}\right), \quad \ldots\ldots\ldots \quad (6)$$

or according to (3):

$$\frac{v}{v_0}=1+\text{A}\frac{l}{a}. \quad \ldots\ldots\ldots \quad (7)$$

Fig. 3.



The slope of the line (7) gives the common constant A, which was likewise at first determined by taking the linear mean and which gave the value 1·04. The largest of the test bodies measured was of radius about $4 . 10^{-5}$ cm., the smallest about $1·9 . 10^{-5}$ cm. The law of resistance, which until now had been proved valid only for larger spheres, hence retains its validity also for this order of magnitude.

§ 4. II. *Exponential law of resistance.*

In a well-known paper, M. Knudsen and S. Weber* determined empirically the mobility of large spheres in gas by means of vibration experiments. They obtained the following formula:

$$B=\frac{1}{6\pi\mu a}\left[1+\frac{l}{a}\left(A+De^{-C\frac{a}{l}}\right)\right], \quad . \quad . \quad . \quad (8)$$

to which F. Ehrenhaft has referred in his publication †. The question is, whether this formula is also valid for our fluid spheres, which lie at the extreme limit of visibility. For this purpose we write B in the form (8). We thus obtain a relation between $\frac{v}{v_0}$ and $\frac{l}{a}$:

$$\frac{v}{v_0}=1+\frac{l}{a}\left(A+De^{-C\frac{a}{l}}\right). \quad . \quad . \quad . \quad . \quad (9)$$

From the circumstance that the slight curvature is concave upwards, as can be seen from fig. 3, it follows that this three-constant formula agrees better with the results of observation. The computation was here carried out in the following manner. Approximate values were at first substituted for the constants A, D, C in formula (9). By this means the problem was reduced according to Gauss' method to the solution of linear equations. As many linear equations result as there are points in fig. 3. The corrected constants obtained in this manner are again substituted in equation (9), and the radii of the test bodies are computed according to Newton's method of approximation. The results are listed in Table II.

Table II.

Test body No. ...	27.	32.	46.	45.	44.	29.	25.
$a_e \cdot 10^5$ cm. ‖	1·962	2·470	2·176	3·574	3·650	3·789	4·212
$a_1 \cdot 10^5$ cm.	1·924	2·418	2·149	3·557	3·676	3·918	4·141

$A=0{\cdot}943.$ $\qquad D=0{\cdot}169.$ $\qquad C=1{\cdot}54.$

‖ a_e marks the radius computed according to the exponential law of resistance, while a_1 is the radius determined by taking the linear mean.

We hence obtain:

$$B=\frac{1}{6\pi\mu a}\left[1+\frac{l}{a}\left(0{\cdot}943+0{\cdot}169e^{-1{\cdot}54\frac{a}{l}}\right)\right]. \quad . \quad (10)$$

---

* M. Knudsen and S. Weber, *Ann. d. Phys.* xxxvi. p. 981 (1911).

† F. Ehrenhaft, *loc. cit.*

If we now compare the results given in Table II. with the values obtained by taking the linear mean, we observe that the difference in value of the radii computed according to the two methods can be as great as 3 per cent. and in the mean does not exceed 1 per cent. According to this it is possible to compute with sufficiently good approximation the sizes of such small test bodies according to the Stokes-Cunningham's law, as has always been done.

§ 5. *The possibility of a Direct Determination of Magnitude.*

The observations were carried out with the illumination aperture 0·3 and the observation aperture 0·3 in an Ehrenhaft condenser with plates of diameter about 9 mm. These fluid droplets were perhaps the smallest which can be observed for the purpose of measurement with this optical apparatus. Mercury droplets might be rendered visible and observable in still smaller sizes, for they have a much greater coefficient of reflexion and, due to their greater density, fall much more rapidly. The problem of the validity of the law of resistance for colloidal mercury spheres is a matter for future experiment.

It would be particularly satisfying to be able to take out such a drop of fluid after observations, to place it upon a microscope slide, and to look at it with a microscope of the highest aperture by direct illumination. Essential difficulties stand, however, in the way. Such a precipitated droplet does not assume a spherical form, but a form computed by F. Neumann *. If we knew the capillarity constants of the fluid and of the glass, we might deduce the weight of the non-moistening drops from the measurements given by F. Neumann. But this procedure would also be hardly applicable to fluids. It, however, affords a means for the determination of magnitude and weight of solid bodies, and might permit of an extension of magnitude determinations by means of the law of resistance below the limits already approached.

§ 6. *Colloidal Gold in a Gas.*

It will then be found necessary to undertake the determination of the magnitude of smaller test bodies of radius less than 2 . 10 cm.$^{-5}$. A very large field of modern physics is concerned with such particles. They are single, colloidal test bodies of a magnitude which runs from $2 . 10^{-5}$ cm. to $5 . 10^{-6}$ cm. and below. Up to the present time Ehrenhaft has used purely optical methods for these test bodies[*]. These methods permitted of the computation of magnitude from the colour of the light scattered by the test bodies, assuming the optical constants of the test bodies as known. The choice of such test bodies is limited by several conditions. For the sake of an easier managing of the test bodies and of the shorter duration of the experiments, it is necessary to choose test bodies of great reflecting power and large density. Finally, we must choose test bodies which remain chemically invariable. Gold in nitrogen would offer a suitable material, as an occlusion or adsorption of the gas would in this case not be expected. F. Ehrenhaft has long ago referred to this selection of experimental material[†].

---

* F. Neumann, Vorl. über d. Theorie d. Kapillarität, Leipzig, 1894.

The production of such test bodies can be undertaken in several ways. They can be produced either in an electrical arc between two gold electrodes of a thickness of 0·5 cm., or by heating finely divided gold powder in a quartz retort[‡]. For the first we applied the later procedure. If, after heating, we pass the stream of gas through the condenser, we see the small gold test bodies as luminous points against a dark background. If many such particles are produced, it is observed that after a time several particles now and then meet and form a coagulum similar to that which is well-known in the case of fluids. We can, however, easily differentiate between the single and the complex particles. For whereas the single particles give rise to a normal diffraction disk[§], the coagula are exceptionally brilliant, exhibit at first sight an irregular form and orient themselves in the electrical field so that the largest dimension falls in the direction of the electrical force. Every experienced microscopist would be able to distinguish the irregular test bodies, which now and then appear only after a considerable lapse of time. This he is able to do the more easily, if, under the same conditions of observation, he applies a larger aperture. In order to get the object plane in the centre of the condenser plates in this case, it is necessary to make use of a condenser of smaller dimensions, with condenser plates of diameter of but 3 mm. F. Ehrenhaft employed such a condenser in his first work. The test bodies are clearly to be recognized as single particles also with this greater aperture. We of course wish to carry on our experiments only on these single test bodies, as the determination of the law of resistance has only in this case any meaning.

---

[*] F. Ehrenhaft, *Phys. Zeits.* xv. p. 952 (1914); xvi. p. 227 (1915), etc.

[†] F. Ehrenhaft, *Phys. Zeits.* xii. p. 263 (1911).

[‡] After a longer heating the retort gets covered within with a reddish sediment of the colloidal gold.

[§] Discussion to the report of F. Ehrenhaft, *Phys. Zeits.* xi. p. 12 (1910) (Siedentopf).

§ 7. *Comparison of the Gold Test Bodies with* $K_4Hg_2I_4$ *droplets, especially with reference to the Brownian Movement.*

We now wish to consider those smaller test bodies of radii below $2 . 10^{-5}$ cm. Let us compare the $K_4Hg_2I_4$ test body no. 32, which, as is known, obeys the law of resistance, with a gold sphere such as referred to. It follows from Einstein's theory of the Brownian movement that the spheres which show the greater Brownian fluctuation have the greater mobility and hence the smaller radius[*].

TABLE III.

$K_4Hg_2I_4$ test body no. 32. Times of fall in sec.

11·28	12·12	10·68	11·46	10·66	13·90	10·76	11·52	10·60	10·34
11·34	10·32	12·34	11·60	13·46	13·30	13·12	10·14	12·50	10·88

Distance of fall: $35{\cdot}0 . 10^{-3}$ cm. $\overline{\lambda^2}$: $0{\cdot}978 . 10^{-6}$.

Au test body no. 10. Times of fall in sec.

12·06	10·88	10·00	17·04	15·18	9·44	12·22	15·18	18·98	13·80
12·68	13·72	6·78	11·90	7·66	22·70	6·32	14·60	8·10	9·02

Distance of fall: $14{\cdot}5 . 10^{-3}$ cm. $\overline{\lambda^2}$: $1{\cdot}963 . 10^{-6}$.

If we now compare the figures given in Table III. for the two test bodies, we notice that the percent. fluctuation of the times of fall is 16·2 per cent. for $K_4Hg_2I_4$ and 51·0 per cent. for gold. The distance of fall of the gold test body is moreover more than half as small as that of the $K_4Hg_2I_4$ drop, from which it would appear that the Brownian fluctuation of the former should be yet smaller. If we determine the mean square displacement per second for the two test bodies, we find for gold the value $1{\cdot}963 . 10^{-6}$, for $K_4Hg_2I_4$ the value $0{\cdot}978 . 10^{-6}$, *i. e.* a value nearly twice as small as for gold. The result of computation that the Brownian fluctuation is in general much greater for gold particles than for $K_4Hg_2I_4$ droplets hence agrees with direct observations. Therefore the radius of the gold particle can at any rate be only as half as great as $2{\cdot}4 \,.\, 10^{-5}$ cm.[*]

---

[*] According to Einstein's Theory: $B=\frac{N}{2RT}\cdot\overline{\lambda^2}$.

We may see, however, from the following circumstances that the Brownian movement can give no decision as to the question of the size of the test bodies. In the first place, let us assume that the possible number of single measurements is sufficient according to the statistical standpoint. One would then conclude that the Brownian movement leads to such important contradictions, that it would not be applicable for our computations. Let us then determine the mean square displacement per second, $\overline{\lambda^2}$, of the same test body at different gas pressures, and let us compute the product of the Loschmidt-Avogadro constant by the weight of the test body, $N \,.\, mg$, separately for each pressure. We make use of the relation:

$$N \,.\, mg = \frac{v}{\overline{\lambda^2}} \,.\, 2RT, \quad . \; . \; . \; . \; . \quad \text{(I)}$$

where v is to be computed from the times of fall and $\overline{\lambda^2}$ from the deviations among them. For one and the same test body the values of $N \,.\, mg$ would remain constant. In this connexion it was proved that the weight of the test body had not changed during the measurement[†]. The values for $N.mg$, however, show rather large fluctuations. For gold test body no. 12 we obtain for $N \,.\, mg$ the following values:

Pressure in mm. Hg ……	751·0	242·3	159·0	751·0
$N \,.\, mg\; 10^{-13}$ ………………	2·67	2·52	3·38	2·58

We notice that the value for $N \,.\, mg$ at low pressure deviates about 26·5 per cent. from that at atmospheric pressure. At lower pressures these deviations are still much greater[‡].

In the second place, let us compute the mobility B in the well-known manner without assuming the density known according to Einstein's relation. If we then set this equal to the mobility resulting from the law of resistance, we obtain:

---

[*] It may be noticed that the $K_4Hg_2I_4$ drops, as well as other particles of the same order of magnitude, which appear in their regular plane of vision as sharp luminous points against a dark background, are also well visible as spherical disks in the neighbouring planes of vision, which according to the size of the particles are more or less remote from each other. In the case of the observed gold test bodies this does not occur. These particles can be made visible only in the plane of distinct vision. This fact may also furnish the evidence that the observed gold test bodies are all smaller than the smallest of the $K_4Hg_2I_4$ drops.

[†] For this test body the balancing potentials E* (see note +, p. 32) are the following: 0·033, 0·030, 0·033, 0·035.

[‡] S. Landman, *Z. f. Phys.* xxvii. p. 237 (1924).

$$B = \frac{N}{2RT} \cdot \bar{\lambda}^2 = \frac{1}{6\pi\mu a}\left(1 + A\frac{l}{a}\right) \quad . \quad . \quad . \quad (II)$$

In this manner we can determine the radius a. On the other hand, we can compute $N \cdot mg$ according to (I). If we now assume that the test body is of spherical form (this can be proved by independent experiments, as will be discussed below), and set therefore

$$N \cdot mg = N \cdot \frac{4}{3}\pi a^3 \sigma g,$$

we can compute the density σ by eliminating the radius from this expression by means of relation (II). If we compute the density of gold in this manner, we obtain for example for test body no. 10 the value 1·2. This result, when considered in conjunction with the proofs for the regular structure and form of the test body carried out further on in this paper, remains entirely inexplicable.

If we assume, however, that the possible number of single measurements is not statistically sufficient, we shall be able to draw no conclusions at all from the Brownian movement, and must leave it out of our computations.

§ 8. *The Law of Resistance for Colloidal Gold.*

We now wish to determine the law of resistance for these colloidal gold particles, and by this means their magnitude. The procedure of measurement and computation is here the same as that applied for $K_4Hg_2I_4$ and described in § 3 of this paper. The problem is indeed more difficult for gold, and because of the smallness of the test bodies cannot lay claim to the same exactness. In Table IV. we see that the radii correspond to the velocities of fall. We also notice the similarity between the diagram of fig. 4, where the velocities of fall are plotted as a function of the pressure (of the mean free path of the molecules, l), and the corresponding diagram for $K_4Hg_2I_4$. Hence we have also here to do with test bodies of the same density. If we now separately determine for each test body the constant A of the law of resistance according to the method given in the first part of this paper, we find the values given in Table IV. We notice, however, that these constants are much smaller than those for $K_4Hg_2I_4$. Thereby we have made use of the normal density of gold.

Fig. 4.

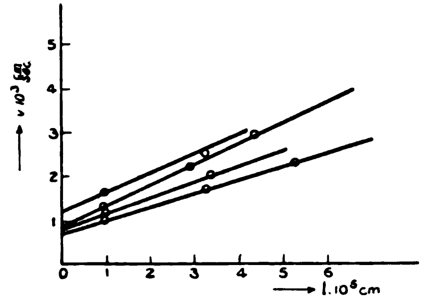


TABLE IV.

Test body No.	$v\,.\,10^3\,\frac{\text{cm.}}{\text{sec.}}$	$v_0\,.\,10^3\,\frac{\text{cm.}}{\text{sec.}}$	β.	$a\,.\,10^5$ cm.	A.	n.
14	0·957	0·711	30·35	0·54	0·23	3
10	1·167	0·811	35·78	0·58	0·25	3
12	1·308	0·870	46·38	0·60	0·32	5
7	1·404	0·881	32·50	0·61	0·22	4
1	1·633	1·293	36·36	0·73	0·20	2

The radii of the gold test bodies are of the colloidal order of magnitude, as has been made plausible by consideration of the Brownian movement. The matter hence takes on an appearance, as if the law of resistance were different for small metallic colloidal test bodies from that for large drops of fluid. We reserve, however, our definite opinion about this matter until we are able to make use of sufficiently great statistical data of other metallic colloidal particles.

Some writers have tried to argue in the reverse way. For, if we consider the density σ as unknown, there are three unknown qualities a, A, σ, present in the two equations (4) and (5). If we then assume the density σ as known, we may compute the radius a and the constant A *. This has been carried out in Table IV. One can, on the other hand, take the value of A from the results obtained from other test bodies, *e. g.* $K_4Hg_2I_8$, and thus determine σ. The result of this method of computation is, however, very improbable. We find in this manner, viz. for gold densities up to 1, *e. g.* for the gold test body no. 10, mentioned above, a density $\sigma = 1{\cdot}7$ and a radius $1{\cdot}95\,.\,10^{-5}$ cm. The question

* F. Ehrenhaft, *Ann. d. Phys.* lxiii. p. 784 (1920). Th. Sexl, *Ber. d. Akad. d. Wiss.* (II *a*), cxxxii. p. 139 (1923).

remains unanswerable, why the single particles of colloidal gold should have a density deviating from that of gold in the bulk.

§ 9. *Capture and Microscopical Observation of the Single Gold Test Body.*

For the purpose of the direct determination of magnitude we now wish to apply the above-described method, which is invalid for fluids, to gold. The applicability is dependent upon the success of making observations of such a single test body of gold, of the isolating it and of examining its form and structure by means of the direct microscopic image. This has for the first time been successfully accomplished. A single test body of the size $5 . 10^{-6}$ cm. and of weight approximately $1 . 10^{-11}$ was observed in the condenser, taken out and measured directly. The following means were employed for this purpose.

A brass cylinder is jointed to an Ehrenhaft condenser with plates of diameter 9 mm. By means of a micrometer-screw a pin can be thrust within. The entire apparatus is made vacuum proof. On the front of the pin there is a small silver leaf of the thickness 0·06 mm., which has in the centre a finely bored hole. A thin piece of glass or quartz of the thickness about 0·1 mm. is fastened below this hole.

At first the test body is put through the usual measurements. the silver leaf is then with the greatest care thrust horizontally within the condenser by means of the micrometer-screw. In order to make the experiments possible we must earth the leaf. The test body is now drawn into the space above the hole of the silver leaf by means of the divided upper condenser plate, which can be brought to another potential at the centre. The particle is then exactly centred and allowed to fall through the hole of the silver leaf upon the piece of glass *. It was frequently impossible to find the single test body on the glass. We often succeeded, however, in throwing a single test body upon the centre of the leaf. When we then took out the leaf and examined it with the dry aperture 0·95, we found the test body sought, but also a second or a third. These other particles are from other planes of vision and fall upon the leaf without being observed during the fall. All these test bodies were nearly of the same size. After they had been located with the dry aperture 0·95, they were examined in direct light and against a dark background with oil-immersion aperture 1·3. They

---

* The cleaned cover-glass was of course microscopically examined with aperture 0·95 before the experiments and found free from particles.

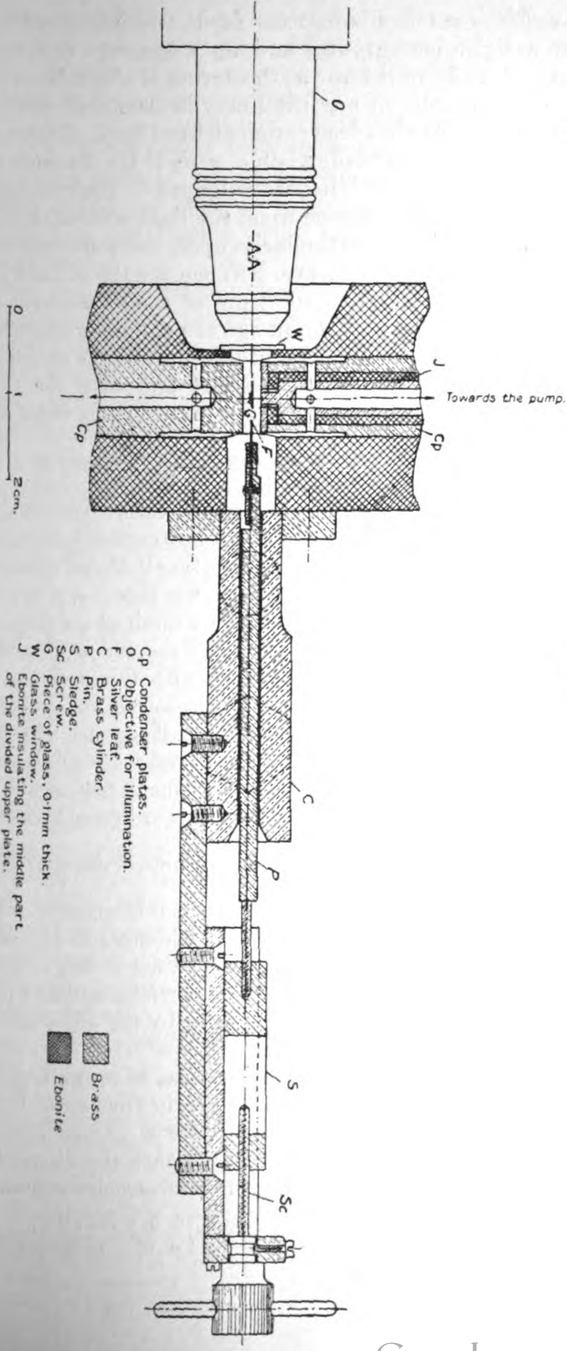

O
A A
W
J
Towards the pump.
G
F
Cp
Cp
0
1
2 cm.
C
P
S
Sc
Cp Condenser plates.
O Objective for illumination.
F Silver leaf.
C Brass cylinder.
P Pin.
S Sledge.
Sc Screw.
G Piece of glass, 0·1mm thick.
W Glass window.
J Ebonite insulating the middle part of the divided upper plate.
Brass
Ebonite

Fig. 5.

then exhibited an isodiametrical form, which appeared dark against a light background and light against a dark background. "As is well known, the action of a microscope for such single particles of any kind may be compared with that of the telescope by the observation of fixed stars. These sorts of objects are always made visible, even if the diameters are less than one-tenth of the wave-length. Their visibility depends among other things upon the light contrast, and for weak shadow effects particularly upon the sensitiveness of the retina of the observer's eye. When the size of the object is appreciably less than a multiple of the wave-length, the diameter and the form of the image are no longer completely determined by the diameter and the form of the object, but depend upon the numerical aperture and upon the wave-length" *. For the distance between two points which may still be resolved in the extreme case is $\frac{\lambda}{2A}$, where λ is the effective wave-length, and A the aperture. We could in fact observe this. For when we microscopically examined one of these test bodies with the aperture 0·95 and attempted to determine the apparent radius, we found *e. g.* a value about $1{\cdot}5 \,.\, 10^{-5}$ cm. When we now examined the same test body in oil-immersion, we found for the radius a value of 0·9 to $1 \,.\, 10^{-5}$ cm. However, even with this aperture the test body did not appear to be fully resolved, but it seemed as if it would be found to be smaller, if we made use of a greater aperture. We could, namely, not yet obtain a sharp image with this aperture †. "For such isodiametric or nearly isodiametric particles always appear as nearly circular disks of diameter $\frac{\lambda}{2A}$, as soon as the actual diameter in all directions is appreciably smaller than this quantity. This behaviour occurs without exception, whether the objects in question appear as light particles against a dark or a less transparent background, or as dark particles against a light field." We could attain both effects by the adjustment of the iris diaphragm.

The findings would therefore indicate, as we worked with visible light, that the test bodies were in any case of radius less than $1 \,.\, 10^{-5}$ cm. If there were a greater aperture for visible light we could actually measure the diameter of the test body. We notice that the microscopic examination of the test body at least furnishes an upper limit for the radius. If we now assign a density 1 to 1·5 to such test bodies, the radius would come out twice as large as the limit indicated by the optical findings.

---

* L. Dippel, *Handb. d. allg. Mikroskopie*, ed. ii. p. 317 (1882).

† We worked also with the aperture 1·3 with fixed dark field diaphragm.

§ 10. *Ultraviolet Photographs of Colloidal Gold.*

We must, however, admit that this question can only then be fully cleared up, when we obtain photographically a real image of the test bodies. This has also been successfully accomplished.

Prof. A. Köhler with C. Zeiss in Jena has, as is known, constructed, according to the computations of v. Rohr, quartz monochromatic microscope objectives of the aperture 1·25, which permit of microscopic photographs of the finest structures. As the resolving power of the microscope increases in proportion as the effective wave-length decreases, we may by applying the greatest aperture 1·25 and ultraviolet light of the wave-length 275 $\mu\mu$ still resolve two points at a distance $1{\cdot}1 . 10^{-5}$ cm. On account of the short wave-length of the ultraviolet light the resolving power becomes as great as the relative resolving power of an aperture 2·50 by daylight. Such an aperture it is impossible to produce with our present means to-day.

One of the writers had such ultraviolet photographs made in our institute. Photographs were at first taken of the algæ "*Surirella gemma*" and "*Pleurosigma angulatum*" with the magnesium line (I. & II., Pl. I.). We will call attention to the comparison of these photographs with that by visible light *.

Prof. A. Köhler in Jena had the kindness to take ultraviolet photographs of small selenium spheres, which Mr. H. Kaiser had produced in Jena according to the Ehrenhaft method. The spheres were let fall upon a quartz plate and immersed in glycerine; the photographs were made with a monochromatic objective of focal length 1·7 mm. and the numerical aperture 1·25 (magnification 1500). From the photographs we see at once that these test bodies retain the spherical form also in submicroscopic sizes †.

---

* F. Ehrenhaft, *Wien. Akad. Ber.* cxxiii. [II *a*], January 1914.

† We wish to express the warmest thanks to Prof. A. Köhler for his production of these photographs. He applied an arc of length 3·5 cm., an alternating current transformer of from 200 volts to 10,000 volts and a condenser of 2 . 10,000 cm. capacity. The potential across the primary of the transformer was 100 volts, the primary current 2·5 A , the source potential 200 volts, and the frequency 50. Current and potential were measured with hot-wire instruments. The ultraviolet light was concentrated by means of a quartz condenser of four lenses with duplex front lens.

Mr. E. Sax * was then induced to produce similar photographs in our institute in Vienna. These photographs also show an exact spherical form. We reproduce the photographs here (IV., Pl. I.), because definite experiments on radioactive Se test bodies were described in Phil. Mag. †, and reference made to the prospective proof of the spherical form.

The photographs of colloidal gold particles (V., Pl. I.), which had been let fall upon a quartz plate and resolved, demand particular interest. For the sake of comparison the Zeiss scale 10^{-3} cm. per division was photographed on the same plate. We notice that all these test bodies are of a colloidal order of magnitude of radii from $5 . 10^{-6}$ cm. to $1 . 10^{-5}$ cm. and possess the spherical form. A single colloidal test body was also photographed. The radius found by these means was $7 . 10^{-6}$ cm., which is in a good agreement with the results from the law of resistance and from the direct optical findings ‡. We may indeed consider the opinion so often expressed that such test bodies do not possess a spherical form as refuted.

Mr. E. Sax has recently succeeded in taking photographs of mercury spheres by means of the ultraviolet light with the wave-length $\lambda=275\ \mu\mu$. The same spot of the preparation with large and small spheres was resolved by varying the planes of vision, the distance between them being removed to $5 . 10^{-5}$ cm. from each other. We would like to draw attention to the different sharpness of the images of the differently sized spheres of radii from $5 . 10^{-6}$ cm. to $5 . 10^{-5}$ cm., as shown in photograph VI. (Pl. I.). The group (1) on the left corresponds to the lowest plane of vision. Each following group corresponds to about $5 . 10^{-5}$ cm. higher plane of vision, being attained by turning the micrometer-screw of the microscope. It should be interesting to compare these series of spherical mercury dorps with the photograph VII. (Pl. I.), which shows non-spherical particles of sulphide of antimony, taken up with the same optical means as the mercury drops.

---

* Our thanks are due to Mr. H. Kaiser, teacher of the "Graphische Versuchsanstalt" in Vienna, and to Mr. E. Sax, cand. phil., for the production of these photographs. The apparatus used in the production of these ultraviolet photographs was similar to that of Prof. A. Köhler. They used the same length of arc, an alternating current transformer of from 110 volts to 10,000 volts, and a condenser of the same capacity as that of Köhler. The potential across the primary was 43 volts, the primary current 5·6 amperes, the source potential 110 volts, the frequency 45.

† *Loc. cit.*

‡ In the original photographs the test bodies are shown so small that a reproduction in a journal would hardly be possible. Mr. H. Kaiser had the kindness to enlarge the photographs about three times, so that the enlargement of the test body is 4300 times.

In the former paragraph we have deduced the fundamental facts concerning the resolving power of the microscope at the limit of the visibility of light, and have made reference to the quoted passages of Dippel's Handbook. It should be emphasized beyond this that the argumentation, concerning the limiting power of the microscope, is carried out in this book under the assumption that, besides the chief maximum, only one neighbouring maximum of the light diffracted by the small body co-operates in the production of the images *. By these means is attained only the so-called "lowest degree of similarity." The microphotographs produced by means of ultraviolet light, however, show that the difference of the form between the spheres (selenium, gold, mercury) and the non-spherical particles (sulphide of antimony) is given very well also to this order of magnitude.

In order to make the state of affairs perfectly clear, we wish to call attention to the following circumstances. All single particles of colloidal gold, for which the law of resistance was determined by evacuation, give for the constant A a value 0·2–0·3. All the test bodies removed from the condenser were isodiametrical and of order of magnitude below the limit which can still be measured by means of the aperture 1·3 in visible light. Finally all test bodies when photographed with ultraviolet light showed an exact spherical form. The measurements made on the ultraviolet photographs, which represented the real images of the test bodies, give the same colloidal magnitude, which, as mentioned above, follows from the law of resistance. It is a matter for the future to carry out these somewhat difficult and extremely tedious experiments on the same test body.

We may therefore be sure that our assumption of the spherical form is the correct one, and that we must draw the conclusions following from this assumption and from the normal density of the test bodies.

The University of Vienna,
November 14, 1925.

APPENDIX.

The fact that a regular law of resistance is found on drops of the "Thoulet"-solution is not isolated, as has been shown by the further experiments in our institute. The law of resistance has since been empirically determined on drops of

---

* *Cf.* E. Abbe, "Die Lehre von der Bildentstehung im Mikroskop," p. 95, Braunschweig, 1910.

a saturated solution of $BaHgI_4$, by means of the same procedure as that on $K_4Hg_2I_4$-drops. By concentrating the solution of $BaHgI_4$ to the state of complete saturation, it could be reached that the test bodies retained the constancy of the mass also at the lowest gas-pressures. Mr. M. Reiss has established the law of resistance for this fluid of the density 3·5 by means of a sufficiently great number of points (130 points, according to diagram 3 of this paper) *.

Not only the sprayed fluid-drops, however, furnish a unitary law of resistance, but also selenium spheres produced by evaporation, the ultraviolet photographs of which we have previously shown. This law for selenium has been set up by Mr. H. Trebitsch in our institute by calculating the results of the observations taken by J. Mattauch. On solid selenium spheres about the same law results, as on the drops of fluids. The twice-repeated computation according to the method of least squares gives for constants of the exponential law of resistance the following values: $A=1{\cdot}034$, $D=0{\cdot}172$, $C=2{\cdot}77$ (conf. equation 10). All these substances of various densities, *i. e.*, oil (0·93), $K_4Hg_2I_4$ (3·01), $BaHgI_4$ (3·50), Se (4·26), therefore give approximately the same relation for the mobility as was obtained quite independently of any assumption concerning the charges of the test bodies.

The problem of the validity of the law of resistance on these test bodies of the order of magnitude to 1.10^{-5} cm. is hence solved. It requires, however, some further examination on metallic test bodies of radii below 1.10^{-5} cm. to 5.10^{-6} cm. For the methods which are to be undertaken in this case we refer to the communication, "Sur l'observation et la mesure des plus petits aimants isolés," which has appeared in the *Comp. Rend.* vol. 182, p. 1138. Paris, 1926.

The *electrostatic charges* of these test-bodies, computed with the law of resistance that has been determined in a purely mechanical way, are especially remarkable. The results obtained on the drops of the $BaHgI_4$-solution of radii from 1·2 to $3{\cdot}2\,.\,10^{-5}$ cm., as well as on selenium spheres of radii from 1·2 to $3{\cdot}5\,.\,10^{-5}$ cm., are still more conspicuous than that on the drops of the $K_4Hg_2I_4$-solution (the charges of the $K_4Hg_2I_4$-drops treated in this paper are the following: 4·34, 3·82, 3·75, 5·12, 4·88, 22·82, $10{\cdot}26\,.\,10^{-10}$ E.S.U.). Among 20 charges measured directly on the $BaHgI_4$-drops, 13 were found to be smaller than $4{\cdot}0\,.\,10^{-10}$ E.S.U.; among 26 charges on selenium spheres 8 are deviating from the electron by more than 20 per cent., the smallest charge being measured to $2{\cdot}80\,.\,10^{-10}$ E.S.U.

---

* The constants of the law of resistance are in this case: $A=0{\cdot}879$, $D=0{\cdot}229$, $C=2{\cdot}61$.

The extensive tables and proofs regarding this communication will be published in the *Zeitschr. f. Physik* in a short time. The objection so often expressed against these charges, that the carriers of them were non-spherical particles of irregular density, can evidently not be made in this case.

By this the problem of the determination of the charges of single small spheres, which has been discussed in the literature of the last 17 years, has been brought to a conclusion.

Vienna, May 18th, 1926.

IV. *The Loud-Speaker as a Source of Sound for Reverberation Work.*

By A. H. Davis, *D.Sc.*, *and* N. Fleming, *B.A.*, *Physics Department, The National Physical Laboratory*[*].

Abstract.

In reverberation work it is important to have a source of sound of which the activity can be varied in a large known ratio. The suitability of a loud-speaker for this purpose has been studied. A loud-speaker actuated by audio-frequency current of pure sine wave form was set up in a room, and measurement was made of the manner in which the intensity of sound at any point in the room varied with the exciting current. The measurements of relative sound intensity were made by means of a condenser microphone with suitable accessory apparatus for measuring the small electromotive forces involved. An electrodynamic type of loud-speaker was found to be satisfactorily constant and free from lag, and over a wide range to have an activity approximately proportional to the square of the exciting current. An electromagnetic instrument tested was, on the whole, less satisfactory. As a further test, measurements were also made of the rate of decay of residual reverberant sound in each of two large rooms, using the loud-speaker as source. The instrument proved convenient in operation, and satisfactory results were obtained. The logarithmic law for the decay of reverberant sound in rooms was established over an intensity range which appears to be about 3000 times as great as that used by W. C. Sabine in directly testing its validity.

In reverberation work, where the rate of decay of sound in a room is estimated from measurements of the duration of audibility after the source has ceased, it is fundamentally necessary to conduct experiments with

---

[*] Communicated by the Authors.

different values of the initial average intensity in the room. In determining the initial reverberant condition of a room—whether auditorium or test-chamber—this measurement is unavoidable. In cases where the acoustic condition of the room is altered in any way—say by the introduction of absorbing materials for test—the changed interference system in the room may alter the output of the source. Consequently, it is not sufficient merely to observe the altered duration of audibility for a single condition of the source, but strictly a repetition of the multiple intensity work is necessary. It is thus important to have a source of sound of which the activity can easily be varied in a known ratio, and it is desirable, in order to obtain accurate measurements, that this ratio should be large. Sabine* used a number of similar organ pipes, but obviously no great range of intensity is attainable by such means unless the number of pipes is inconveniently large. Moreover, Sabine † found that, unless his pipes were placed at a considerable distance apart, they reacted upon one another, and the total activity of *n* pipes was by no means *n* times the activity of one sounded alone.

Experiments have been carried out to determine the suitability of a loud-speaker as a source of sound in reverberation work, for with a single instrument of this type a great range of activity is readily obtained by varying the current through its coils. For a given position in the room and for a given wave-length the acoustic impedance of the space into which the loud-speaker operates is fixed. Under these conditions, with a satisfactory instrument, the activity will remain constant for a constant current input, and for simplicity it is desirable that the activity be proportional to the square of the current.

I. STUDY OF THE LOUD-SPEAKER AS A SOURCE.

Method of Experiment.

If a source of sound of constant frequency is placed in a closed room, a stationary system of waves is set up which remains fixed so long as the wave-length remains constant. The sound intensity varies from point to point in the room, but at any one point it remains constant for a source of constant activity. If, as is usually assumed, the energy absorbed on reflexion by the walls is always directly proportional to the intensity of the incident sound wave, and unless any degradation of sound energy into heat in the air itself is more pronounced for loud sounds than for feeble ones *, the intensity at any point in the room will be directly proportional to the activity of the source.

---

* Sabine, 'Collected Papers,' Paper No. 1, Harvard Univ. Press, 1922.
† Sabine, *loc. cit.* See also p. 83.

In the present experiment a loud-speaker was used as the source of sound, and a microphone, placed at some other point in the room, served to measure the relative values of the intensity set up at that point. Measurements were made both with an electromagnetic loud-speaker and with one of electrodynamic type. Three types of microphone were used, working respectively on electrostatic, electromagnetic, and electrodynamic principles. The e.m.f. generated by the electrostatic microphone is, for small amplitudes, directly proportional to the amplitude; the sensitivity varies little with time and, in particular, the variation with temperature is quite negligible †. With the other two types for small amplitudes the e.m.f. is directly proportional to the velocity of the diaphragm and therefore, in general, to the pressure in a harmonic sound wave. Thus, in all cases the e.m.f. gives a measure of the sound amplitude at the position of the microphone.

Apparatus.

A diagram of the apparatus used is given in fig. 1. The oscillatory current to actuate the loud-speaker S was generated by a valve oscillator P, and amplified and purified by the tuned amplifier Q, which consisted of four valves of the L.S. type, connected in parallel. The loud-speaker circuit, which contained a thermal milliammeter A_1 and a rheostat R, was inductively coupled to this oscillator unit. A low-resistance (120 ohm) loud-speaker was used, and it was possible to obtain currents of more than 100 m.a. r.m.s. at all frequencies from 125 to 2000 vibrations per second. The wave form of the current was investigated by means of a cathode ray oscillograph, and in all cases a pure sine wave was obtained at each frequency throughout the range of currents employed.

---

* It is generally believed that very loud sounds such as those from fog-horns, etc., suffer very pronounced degradation. Hart (Roy. Soc. Proc. cv. p. 80 (1924)) in the case of sound of very low frequency (100) claims to have measured appreciable degradation of this type at much feebler intensities. This conclusion has not yet been confirmed.

† Wente, Phys. Rev. x. p. 39 (1917); Phys. Rev. xix. p. 498 (1922).

The microphone T was connected—via a connexion unit C in the case of the electrostatic type—through a two-way switch K to the input of the amplifier system U.V. The output of the amplifier system was connected through an iron core transformer to a vacuo junction and galvanometer G. A galvanometer deflexion was thus obtained, the magnitude of which was a measure of the small e.m.f. generated by the microphone.

Fig. 1.

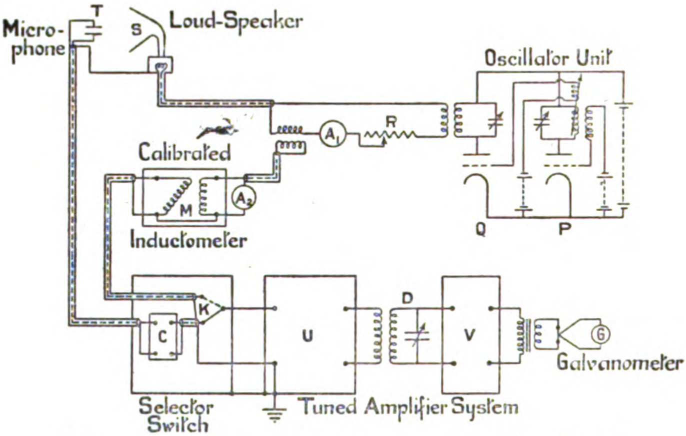


Diagram of arrangements for measuring intensity of sound from loud-speaker.

To determine the actual value of this e.m.f. a substitution method was adopted. By means of the key K a known variable e.m.f. from the mutual inductometer M could be substituted for that from the microphone, and its magnitude could be adjusted until an equal galvanometer deflexion was obtained. The current through the primary circuit of the inductometer was measured by the milliameter A_2, and was obtained by inductive coupling to the main loud-speaker circuit: in consequence of this arrangement, the two equal e.m.fs. from microphone and inductometer respectively were identical in frequency, and the characteristics of the amplifier system UV were thus eliminated. The amplifier system was nevertheless carefully constructed, and was composed of resistance capacity units designed to deal faithfully with the inputs obtained.

Precautions were taken to avoid leaks, and to suppress electromagnetic and electrostatic interference from outside sources. The oscillator was situated as far as possible from the rest of the apparatus, and its coils were so oriented that their electromagnetic fields were without effect upon the measuring system. The sharply tuned circuit D in the amplifier system helped to filter out leaks arising from extraneous sources. This amplifier system and its input switch etc. were screened in metal boxes, and leads to the amplifiers from the microphone and inductometer were shielded. Indeed, the whole of the amplifier and all leads to the grid of the first valve could be regarded as enclosed in the leads to the earthed filaments of the valves. The leads to the loud-speaker were shielded and, with the case of the loud-speaker, were suitably earthed. With these precautions leaks were reduced enormously : the slight residual leak, equivalent in general to an input of the order of 10 micro volts, was usually quite negligible.

Experimental Procedure.

Very early in the work it was found to be vitally necessary to keep the frequency constant in order to avoid any shift of the interference system in the room, and the consequent change in the intensity at the position of the microphone. Great care was therefore taken of this point, and the frequency was tested and adjusted, if necessary, before each reading. But, even though the frequency remain constant, the interference system will change if the temperature of the room varies, since the velocity of sound, and therefore its wave-length, varies with the temperature. In testing the constancy of a loud-speaker over a considerable period the temperature of the room should therefore be kept constant. It was not possible, however, to control this temperature, but some idea of the magnitude of the change to be expected from change of temperature was obtained by altering the frequency by an appropriate small amount. To eliminate the effect of any such temperature drift when measuring the proportionality of loud-speaker output to exciting current, readings for a standard current were taken alternately with the readings for other currents.

Results.

Let i and i' be respectively the current through the loud-speaker and that through the primary of the standard mutual inductance. Since the coupling between these two circuits is fixed, at any given frequency i' is proportional to i, and we may write

$$i' = k_1 i.$$

Corresponding to the loud-speaker current i, let a be the sound amplitude at the position of the microphone, E the e.m.f. generated by the microphone, and M the reading of the mutual inductance when a balance is obtained.

Further, let a_0, E_0, M_0 be values corresponding to a standard current i_0. Since the e.m.f. generated by the microphone is equal to that applied to the amplifier from the secondary of the standard mutual inductance, we have for a frequency n $(=\omega/2\pi)$,

$$E = M\omega i' = M\omega k_1 i,$$

whence

$$\frac{E}{i} = M\omega k_1.$$

If the e.m.f. generated by the microphone is proportional to the amplitude of the sound which excites it, we may then write

$$\frac{a}{i} \propto M\omega k_1$$

or

$$\frac{a}{i} = k_2 M. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the standard value of the current this becomes

$$\frac{a_0}{i_0} = k_2 M_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Choosing arbitrary units so that the sound amplitude per unit current is unity for the standard current, *i. e.* putting $k_2 = \frac{1}{M_0}$,

we have

$$\frac{a}{i} = \frac{M}{M_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If the acoustical activity (energy units) of the loud-speaker is proportional to the square of the exciting current, the sound amplitude at the microphone should be proportional to the loud-speaker current. Consequently, in this case, provided the microphone e.m.f. is proportional to the sound amplitude, $\frac{M}{M_0}$ should remain constant and equal to unity as the loud-speaker current is varied.

Preliminary tests.—If the condition of simple proportionality is satisfied by the microphone, it is to be expected that the form of relation between M/M_0 and i will be the same whether it is obtained with the microphone close to the loud-speaker, in a position of relatively high intensity, or at a distance in a position of relatively low intensity. Experiments were therefore conducted at a frequency of 500 vibrations per sec. with the microphone in different parts of the room in positions of widely differing intensity.

When an ordinary electromagnetic telephone receiver was used as a microphone it was found that in positions of high intensity the value of $\frac{M}{M_0}$ fell off considerably for high currents, whereas in positions of low intensity the fall was not nearly so pronounced. An electrodynamic type—actually part of a commercial loud-speaker movement—also gave different curves in different parts of the room, but in this case the value of $\frac{M}{M_0}$ fell off for low values of the loud-speaker current. The magnitude of this effect could be decreased by more accurately centreing the coil between the magnetic pole pieces and, though the commercial instrument used could not be made quite satisfactory, it is possible that a precision instrument of this type would be.

The condenser microphone, however, showed no such changes. The curves obtained in five different positions in the room, varying from 1 inch in front of the mouth of the loud-speaker horn to over 8 feet away, did not vary from the mean by more than the experimental error.

This result is also of interest in its bearing upon the question of degradation of sound of the type studied by Hart*. If, at this loudness and frequency, such degradation were appreciable, the values of $\frac{M}{M_0}$ should fall off for the higher currents more when the microphone is at a distance from the loud-speaker than when it is close to the mouth of the horn. Since no such behaviour was shown, although the range of intensities used was much greater than that used by Hart, it must be assumed that at this frequency, at any rate, there is no appreciable degradation.

---

* Hart, Proc. Roy. Soc. cv. p. 80 (1924).

In obtaining the results given below the condenser microphone was always used. Since it is less sensitive than the other types, it was placed close to the mouth of the loud-speaker horn to increase the accuracy of the readings for the low values of the loud-speaker currents.

Electromagnetic type of loud-speaker.—When the loud-speaker current was first switched on the amplitude of the sound emitted from the electromagnetic instrument did not immediately assume a steady value, but continued to increase for some time. This effect was more marked with high currents, as long as twenty minutes being necessary before the increase became imperceptible. When this state had been reached stopping the current for a few seconds did not result in a return to the original condition. The phenomenon appears to be due to the local heating effect of the current in the coils of the loud-speaker, which may result in the pole pieces being brought closer to the diaphragm and so give an increase of efficiency.

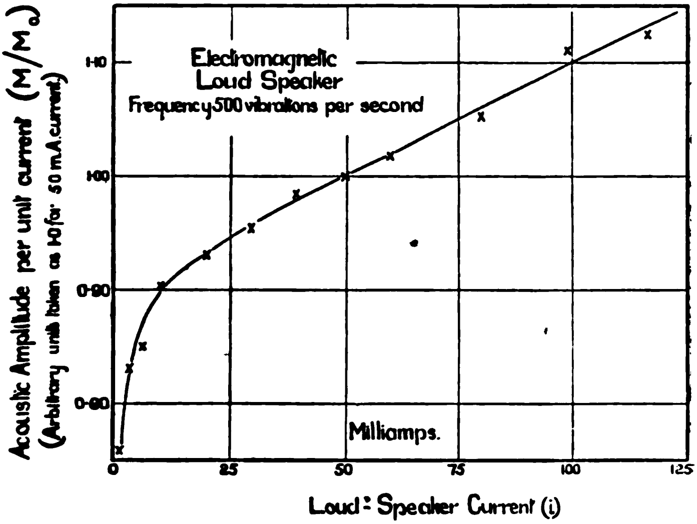
This heating effect was again apparent when the effect of altering the loud-speaker current was studied. On changing to a high current from a low one the efficiency was at first unchanged, but rose gradually for some time; the opposite effect occurred when the current was again reduced.

Usually throughout any period of several hours, during which the current remained constant, the temperature of the room rose and the sound amplitude at the microphone drifted continuously, the sign of the drift being dependent upon the position in the room. The effect was almost competely explained in sign and magnitude by the shift of the interference system in the room, due to the effect of temperature upon wave-length. After allowance was made for this, there was a very slight residual effect representing a decrease of efficiency of the loud-speaker when its general temperature was raised.

The curve finally obtained for the relation between the loud-speaker current and the sound amplitude per unit current, for a frequency of 500 vibrations per second, is given in fig. 2. It shows that the efficiency increases with the current. The very pronounced fall indicated for very low currents is in a region where measurement was difficult, and where small leaks to the amplifier may have become appreciable. Nevertheless, it is thought to be real.

Owing to the long time taken by this loud-speaker in settling down to a steady output, it does not seem very suitable for reverberation work. Further, the increased efficiency at high current strengths, while not of any importance in the normal working of a loud-speaker, is too great for the instrument to be completely satisfactory for the special purpose in view.

Fig. 2.



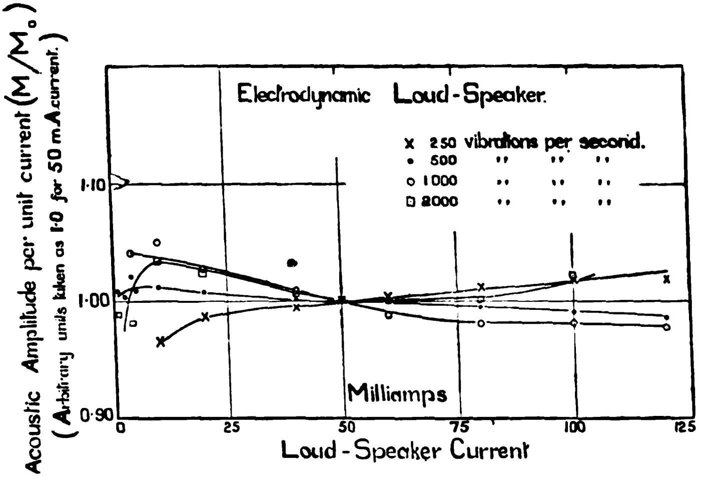
Relation between loud-speaker current and acoustic amplitude per unit current. (Electromagnetic loud-speaker.)

Electrodynamic type of loud-speaker.—The electrodynamic loud-speaker was of the type in which a coil of wire attached to a diaphragm moves in the field of an electromagnet. For constancy it was naturally necessary to maintain the current through the field coils of the magnet at a constant value. A ten per cent. change in current strength resulted in a five per cent. change in the estimated sound amplitude.

As a loud-speaker the instrument assumed its final steady output immediately the audio frequency input was supplied. In any long series of readings for a constant value of this input, the sound amplitude at the microphone drifted continuously since the temperature of the room did not remain constant. With this instrument the drift appeared to be due almost entirely to shift in the interference system in the room arising from the changed temperature. Certain irregular variations from the general drift, of the order of 1 to 2 per cent., were due most probably to very slight errors in tuning.

The curves given in fig. 3 show the relation between

Fig. 3.



Relation between loud-speaker current and acoustic amplitude per unit current *. (Electrodynamic loud-speaker.)

the current and the sound amplitude per unit current (M/M_0) for four different values of the frequency. Again there is evidence of falling off in the efficiency for very low currents though, as above stated above, the measurements in this region are least reliable. Throughout the wide range of currents employed, however, the maximum variation of $\frac{M}{M_0}$ is only $2\frac{1}{2}$ per cent. in the best case ($n=500$) and 6 per cent. in the worst ($n=250$). It may be shown that the error introduced in reverberation

---

* From a static calibration of the condenser microphone it is estimated that, at the mouth of the loud-speaker horn, the sound amplitude per milliamp. loud-speaker current had the values 1/30, $\frac{1}{5}$, 1/8, $\frac{1}{4}$ dynes per sq. cm. for frequencies of 250, 500, 1000, 2000 v.p.s. respectively.

measurements by assuming constant efficiency is quite small[*].

The electrodynamic loud-speaker thus appears to be generally satisfactory for reverberation work. In precision measurements in very reverberant rooms it would be necessary to allow for the variations indicated by the curves: the allowance has not been made in this paper.

II. USE IN REVERBERATION WORK.

The loud-speakers tested were used in reverberation work to determine the rate of decay of sound in a room. Briefly the method is to determine the duration of audibility in the room after the source is stopped, and then to repeat the experiment with a source of n times the activity. The difference observed is the time in which the sound in the room decays n fold. By conducting a whole series of tests it is possible to determine whether the decay factor for the room is the same for sounds of different initial intensity. This was done by Sabine[†] over a restricted range, up to about 4-fold, in his multiple organ pipe work. He found that the decay of sound of a given pitch in a room obeyed the logarithmic law,

$$\log \frac{I}{I_0} = At, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where I is the average intensity at the moment when the source is stopped and I_0 the average intensity at time t later, and A is a constant independent of the intensity of sound. Taking I_0 to be the minimum intensity necessary for audibility, and remembering that in the present case the original value of the average intensity is proportional to the square of the current through the loud-speaker, we may write

$$\log \frac{ki^2}{I_0} = At,$$

or

$$\log i = \tfrac{1}{2}At + \text{const.}, \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

where t is now the time required for the average intensity to fall to the minimum necessary for audibility or briefly the duration of audibility. There should thus be a linear relation between the loud-speaker current, plotted logarithmically, and the duration of audibility. From this the decay factor A for the room may be obtained.

---

[*] An error of 10 per cent. in an intensity ratio of 100^2 : 1 corresponds to a 1 per cent. change in the time taken for the reverberant sound in a room to decay in this ratio. For any but rooms of very long period this is of the order of the experimental error in the determination of audibility duration.

[†] Sabine, 'Collected Papers,' Paper No. 1, Harvard Univ. Press, 1922.

Apparatus.

The arrangement of the loud-speaker and its source of alternating current was identical with that shown in fig. 1. A key was arranged which, when depressed, stopped the loud-speaker by breaking the high-tension circuit of the oscillator, and simultaneously started a time recorder. A second key was used in recording the instant at which the audibility was judged to cease in the chamber.

The loud-speaker was placed in the room under investigation, whilst the recording apparatus was situated outside. A position was chosen for the loud-speaker well away from all the walls and not directly facing any one, in order to minimise as far as possible any reaction effects. In one particular case the room appeared to have a resonance frequency very near—within, say, 1 vibration in about 2 seconds—to the frequency with which it was desired to work, and, owing to reaction upon the loud-speaker, considerable difficulty was experienced in tuning. Beats occurred which persisted for some time and then suddenly ceased. By slightly moving the loud-speaker the effect was suppressed, and the phenomenon did not recur at other frequencies tested.

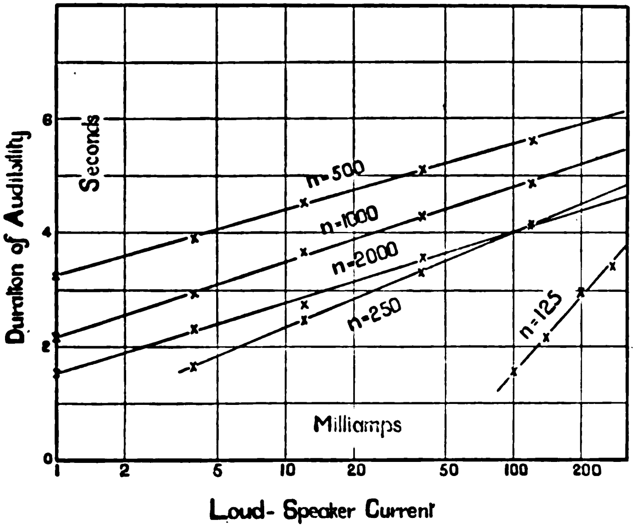
The current was adjusted to a suitable high value, and ten readings were made of the duration of audibility. The sets of measurements were then repeated several times, using successively smaller values of the current. Finally the whole series was repeated in the reverse order, thus finishing up with the high current series with which the experiment was started. By this procedure the effect of any regular change in the efficiency of the loud-speaker due to change of temperature is eliminated. Several series of such readings were taken by two observers and in various positions in the room.

Results.

Measurements have been made in two different rooms. The first room had a volume of about 48,000 c.ft., a concrete floor and ceiling, and brick walls with a large area of windows. It contained several pieces of machinery and some heaps of loose sand which made the exposed surfaces irregular in shape and miscellaneous in character. The electrodynamic loud-speaker was used in this building.

The work in the second room* was done much earlier with an electromagnetic type of loud-speaker, but the results are included here because of the greater simplicity of the structure of this room. It was quite empty and had a volume of about 9620 c.ft., a concrete floor, plaster ceiling, and brick walls with no windows. In neither case were the conditions very favourable for accurate reverberation work, since silence could not be obtained.

Fig. 4.



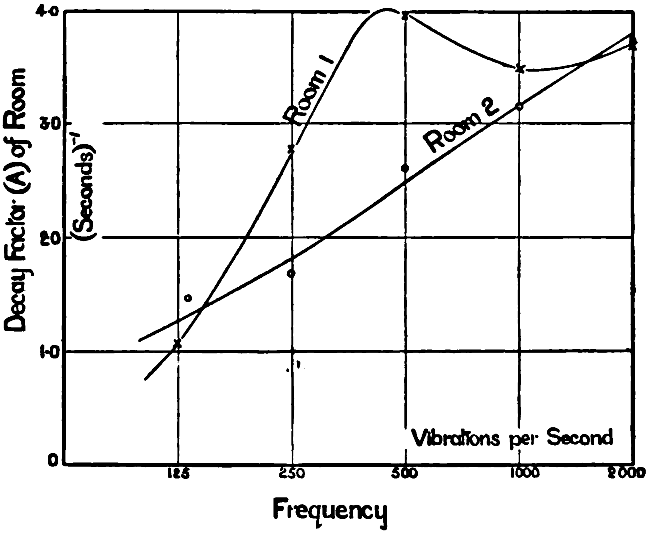
Relation between duration of audibility and loud-speaker current in room 1.

Fig. 4 shows the relation in room 1 between the logarithm of the loud-speaker current, and the duration of audibility for different values of the frequency. In most cases the current has been varied over a range of 120 fold, corresponding to a variation of the initial average intensity of over 14,000 fold. Over this wide intensity ratio the logarithmic relation, established by Sabine over a very restricted range, is still found to hold good.

---

* We are indebted to the Director of the Building Research Board for permission to use this room.

Fig. 5.



Relation between decay factor of room and frequency.

The values of the constant A obtained from the curves of fig. 4 are shown plotted against the frequency in fig. 5, together with those obtained in room 2. While there appears to be no simple relation in the case of the first room, in the case of the second room, whose absorbing surfaces were not of such a miscellaneous character, a regular variation with the frequency was obtained.

V. *On the Calculation and Application of High Resistances of small Self-Inductance for all Frequencies.* By RAYMOND M. WILMOTTE, *B.A.* (*of the National Physical Laboratory*) *.

ABSTRACT.

IN many accurate measurements it is necessary to know the exact phase-angle of high resistances of the order of several thousand ohms. In this case the capacity effects are often very large. In the paper, formulæ are given for the self-inductance of high resistances formed by long parallel wires of circular cross-sections and screened from earth by a cylindrical metal shield.

The formulæ for the use of such a standard as a ratio arm and potential divider are also given, together with its application in bridges.

I. INTRODUCTION.

THE use of high resistances in alternating-current measurements often leads to difficulties, owing to the residual self-inductance and the effect of capacity on the circuit. These effects become more pronounced as the frequency increases, and the effect of capacity, which is quite negligible for low resistances, usually becomes predominant when the resistance reaches values of several thousand ohms.

It has been usual to take as a standard of comparison of residual inductance a single long loop of wire with parallel sides, the formula for which was given by S. L. Brown †. It will be shown, however, that this formula only holds in practice if the middle point of the loop is at earth potential—a condition which does not usually obtain.

For high resistances a single loop of wire means a very cumbersome standard, and in this paper formulæ are obtained for a standard made of a large number of long parallel wires connected as shown in fig. 1, where the wires are not necessarily in the same plane. It is necessary, especially for high resistances, to screen the wires from the earth by means of a cylindrical metal shield.

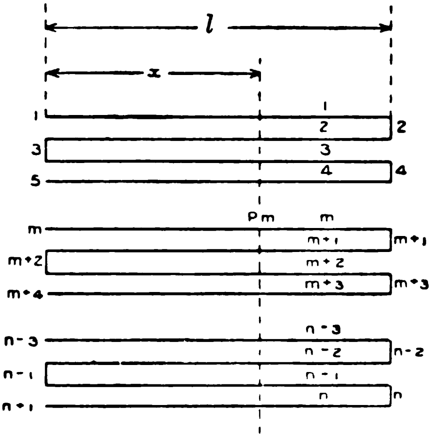
The adaptation to high voltages is complicated, since a very considerable length of wire is required from the necessity of keeping down the temperature rise. For these purposes voltages of the order of 2 to 10 per metre length of wire are commonly used, the current being 0·1 ampere or less. There is also the limitation imposed by the effect of the production of corona around the wire, due to the electric field between it and the shield. These considerations would require a number of systems of the type suggested to be put in series for high voltages. A phase displacement would result, depending upon the capacity and voltage of the different shields to earth. This effect can, however, be calculated if the capacities of the shields to earth are known (either by measurement or by surrounding the whole with a large concentric screen connected to earth and calculating the capacities). In this connexion, when dealing with commercial frequencies, non-inductive resistances for high voltages can be constructed more satisfactorily by the method described by E. Orlich and H. Schultze *, which is more compact and allows of easier computation but is not suitable for higher frequencies.

---

* Communicated by the Author.

† Phys. Rev. vol. xxix. p. 369 (1909).

Fig. 1.



Formulæ are also given for the use of the standard as ratio arms and as potential divider, and it is hoped that they may be found useful at audio frequencies and in developing bridge methods suitable for radio frequencies.

---

* *Archiv. f. Elek.* vol. i. p. 1 (1912).

II. CAPACITY COEFFICIENTS OF n THIN PARALLEL WIRES WITHIN A CYLINDER.

The problem of the capacity between infinite parallel cylinders has not been completely solved, but an approximate solution can be found if the radii of the cylinders are small compared with their distances apart.

Consider n parallel thin conductors of radii $r_1, r_2, \ldots, r_n$ having polar coordinates (a_1, θ_1), (a_2, θ_2), …, (a_n, θ_n) referred to the centre of the cylindrical metal screen of radius R as origin. The image of the wire A_r in the screen will be B_r, where $OB = R^2/a_r$.

Let $q_1, q_2, \ldots, q_n$ be the charges on the wires, the potentials of which are $v_1, v_2, \ldots, v_n$ respectively. We shall assume the dielectric constant to be unity.

Then, the potential of the screen will be given by

$$v_s = C - 2\sum_{r=1}^{r=n} q_r \log (a_r/R), \quad \ldots\ldots \quad (1)$$

and the potential at the surface of the wire of radius r_m surrounding A_m is, if r_m is small, approximately given by

$$r_m = C + 2q_m \log\left(\frac{R^2 - a_m^2}{a_m r_m}\right) + 2\sum_{=1}^{r=n} q_r \log\left(\frac{A_m B_r}{A_m A^r}\right), \quad . \quad (2)$$

in which the term having $r = m$ is left out in the last sum.

If the screen is connected to earth, we have

$$v_m = 2q_m \log\left(\frac{R^2 - a_m^2}{R r_m}\right) + 2\sum_{r=1}^{r=n} \log\left(\frac{a_r \,.\, A_m B_r}{R \,.\, A_m A_r}\right). \quad . \quad (3)$$

The potential coefficients are, therefore, given by

$$p_{m.m} = 2 \log \{(R^2 - a_m^2)/R r_m\} \quad \ldots\ldots \quad (4)$$

$$\text{and} \quad p_{m.r} = 2 \log \{(a_r \,.\, A_m B_r)/R \,.\, A_m A_r\}. \quad \ldots \quad (5)$$

If R is large compared with a, so that a^2 can be neglected compared with R^2, these become

$$p_{m.m} = 2 \log (R/r_m) \quad \ldots\ldots \quad (6)$$

$$\text{and} \quad p_{m.r} = 2 \log (R/A_m A_r). \quad \ldots\ldots \quad (7)$$

Since r is small compared with a, $p_{m.m}$ will usually be greater than $p_{m.r}$ unless R is infinite, when in the limit $p_{m.m} = p_{m.r}$.

The capacity coefficients are given by

$$k_{m.r} = \mathrm{D}_{m.r}/\Delta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

$$\Delta = \begin{vmatrix} p_{1.1}, & p_{2.1}, & \ldots, & p_{n.1}, \\ p_{1.2}, & p_{2.2}, & \ldots, & p_{n.2}, \\ \cdot & \cdot & \cdot & \cdot \\ p_{1.n}, & p_{2.n}, & \ldots, & p_{n.n}, \end{vmatrix} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and $\mathrm{D}_{m.r}$ is the minor of $p_{m.r}$ in this determinant.

Now these coefficients can be exactly represented by capacities $\mathrm{K}_{0.m}$ between any wire m and earth and $\mathrm{K}_{m.r}$ between any two wires m and r, where

$$\mathrm{K}_{0.m} = \sum_{r=1}^{r=n} k_{m.r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\text{and} \quad \mathrm{K}_{m.r} = -k_{m.r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Where there are a number of wires, the determinant of equation (8) becomes unmanageable except in special cases.

If $p_{m.r}$ is small compared with $p_{m.m}$ we have, neglecting small quantities of the second order,

$$k_{m.r} = -\frac{p_{m.r}}{p_{m.m} \cdot p_{r.r}} + \sum_{q=1}^{q=n} \left\{ \frac{p_{q.m}\, p_{q.r}}{p_{q.q}\, p_{m.m}\, p_{r.r}} \right\}, \quad . \quad . \quad (11)$$

in which $q \neq m$ or r and $p_{m.r}$ becomes negative, if $r = m$.

Now suppose all the wires to be distributed along the surface of a cylinder of radius a concentric with the shield and parallel to its axis. Let $\mathrm{R}/a = 1 + \rho$, where ρ is small. Equations (4) and (5) become

$$p_{m.m} = 2 \log \left\{ \frac{\rho(2+\rho)a}{(1+\rho)\, r_m} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\text{and} \quad p_{m.r} = \log \left\{ 1 + \left[\frac{\rho(2+\rho)}{2(1+\rho) \sin \frac{1}{2}\theta_{m.r}} \right]^2 \right\}, \quad . \quad (13)$$

$$\text{where} \quad \theta_{m.r} = \theta_r - \theta_m. \quad .$$

Table I. gives the values of $p_{m.r}$ for various values of ρ and $\theta_{m.r}$, from which we can see when $p^2_{m.r}$ can be neglected compared with $p^2_{m.m}$, since the value of $p_{m.m}$ will usually be between 5 and 15 :—

TABLE I.

Values of $p_{m.r}$.

$\theta_{m.r} =$	5°.	10°.	15°.	20°.	30°.	45°.	60°.	90°.	120°.	180°.
$\rho =$ 0·05	0·814	0·267	0·134	0·078	0·035	0·016	0·010	0·006	0·004	0·002
0·10	1·76	0·791	0·429	0·248	0·128	0·062	0·035	0·019	0·012	0·010
0·15	2·44	1·27	0·764	0·497	0·260	0·126	0·076	0·039	0·029	0·021
0·20	2·93	1·67	1·09	0·746	0·409	0·208	0·128	0·064	0·045	0·035
0·30	3·63	2·33	1·64	1·21	0·718	0·396	0·254	0·136	0·091	0·070
0·40	4·13	2·81	2·07	1·59	1·01	0·592	0·388	0·215	0·147	0·114
0·50	4·53	3·17	2·41	1·91	1·28	0·784	0·531	0·298	0·211	0·163

If ρ is small we can expand equation (13) and obtain

$$p_{m.r} = \frac{\rho^2}{\sin^2(\frac{1}{2}\theta_{m.r})}\left\{1-\rho+\frac{\rho^2}{2}\left(\frac{5}{2}-\frac{1}{\sin^2(\frac{1}{2}\theta_{m.r})}\right)+\dots\right\}.$$

Hence, neglecting small terms of the second order,

$$\mathrm{K}_{m.r} = \frac{1}{p_{m.m}\,p_{r.r}}\left\{\frac{\rho^2(1-\rho)}{\sin^2(\frac{1}{2}\theta_{m.r})} - \rho^4\sum_{q=1}^{q=n}\left[\frac{1}{\sin^2(\frac{1}{2}\theta_{m.q})\sin^2(\frac{1}{2}\theta_{r.q})p_{q.q}}\right]+\dots\right\}, \quad (14)$$

in which $q \neq m \neq r$.

If all the wires are of the same radius r, so that

$$p_{m.m} = p_{r.r} = \dots \equiv p,$$

we have

$$\mathrm{K}_{0.m} = \frac{1}{p}\left\{1+\frac{\rho^2(1-\rho)}{p}\sum_{q=1}^{q=n}\frac{1}{\sin^2(\frac{1}{2}\theta_{m.q})}\right\} \quad . \quad . \quad (15)$$

and

$$\mathrm{K}_{m.r} = \frac{1}{p^2}\left\{\frac{\rho^2(1-\rho)}{\sin^2(\frac{1}{2}\theta_{m.r})} - \frac{\rho^4}{p}\sum_{q=1}^{q=n}\left[\frac{1}{\sin^2(\frac{1}{2}\theta_{m.q})\sin^2(\frac{1}{2}\theta_{r.q})}\right]\right\}, \quad . \quad (16)$$

in which as before $q \neq m \neq r$.

If $p_{m.r}$ is sufficiently small, the last term in equation (16) can be neglected. It should also be noticed that for this $\mathrm{K}_{0.m}$ has the same value for all the wires.

III. STANDARD RESISTANCE.

(a) *General Theorem for* n *Impedances in Series.*

Consider n impedances Z_1, Z_2, ..., Z_n connecting the points 1 and 2, 2 and 3, ..., n and $(n+1)$ respectively.

The point 0 will be assumed to be at earth potential. Suppose the ends of these impedances be interconnected by capacities, the capacity connecting the points m and r being $C_{m.r}$. It is required to find the impedance of the whole, when the capacities are sufficiently small that their products can be neglected.

There will be two definitions of this impedance: one Z_0 will be the ratio of the potential difference across the whole network and the current entering at the point 1 excluding the earth-current to the network, and Z_1 will be the same but including the earth-current. In other words, the impedance will be Z_0 if the current is measured between the points 0 and 1, and Z_1 if the points 0 and 1 are on the same side of the point where the current is measured.

Let $i_1, i_2, \ldots, i_n$ be the currents and $V_1, V_2, \ldots, V_n$ be potentials across $Z_1, Z_2, \ldots, Z_n$ respectively. For shortness, we shall express the sum of these potential differences and impedances between the points m and r by $V_{m.r}$ and $Z_{m.r}$ respectively, so that

$$Z_{m.r+1} = \sum_{p=m}^{p=r} (Z_p) \quad \text{and} \quad V_{m.r+1} = \sum_{p=m}^{p=r} (V_p),$$

where $Z_{m.r}$ and $V_{m.r}$ are positive if $r > m$, and *vice versa*.

$$\text{Now} \qquad V_m = Z_m \, . \, i_m \qquad \ldots \ldots \quad (17)$$

$$\text{and} \qquad i_0 = i_m + \sum_{p=1}^{p=m} \sum_{q=0}^{q=n+1} (V_{p.q} C_{p.q}) \alpha \quad \ldots \quad (18)$$

$$\text{and} \qquad i = i_m + \sum_{p=0}^{p=m} \sum_{q=0}^{q=n+1} (V_{p.q} C_{p.q}) \alpha, \quad \ldots \quad (19)$$

where i_0 and i are the currents entering the network, excluding and including respectively the earth-current, and $\alpha = \omega\sqrt{-1}$, the frequency being $\omega/2\pi$.

From these three equations, neglecting small quantities of the second order, we have

$$V_m/i_0 = Z_m - Z_m \sum_{p=1}^{p=m} \sum_{q=0}^{q=n+1} (Z_{p.q} C_{p.q}) \alpha \quad \ldots \quad (20)$$

$$\text{and} \qquad V_m/i = Z_m - Z_m \sum_{p=0}^{p=m} \sum_{q=0}^{q=n+1} (Z_{p.q} C_{p.q}) \alpha, \quad \ldots \quad (21)$$

in which $Z_{p.q}$ is negative if $p > q$, and *vice versa*.

Since

$$\sum_{m=1}^{m=n}\left\{Z_m\sum_{p=1}^{p=m}\sum_{q=0}^{q=n+1}(Z_{p.q}C_{p.q})\alpha\right\}$$

$$=\sum_{p=1}^{p=n+1}\sum_{q=p+1}^{q=n+1}(C_{p.q}Z_{p.q}^2)\alpha-\sum_{m=1}^{m=n+1}(C_{0.m}Z_{0.m}Z_{m.n+1})\alpha,$$

the impedance of the network is given by

$$Z_0=\sum_{m=1}^{m=n}(V_m/i_0)$$

$$=Z_{1.n+1}-\left[\sum_{p=1}^{p=n}\sum_{q=p+1}^{q=n+1}(C_{p.q}Z_{p.q}^2)-\sum_{p=1}^{p=n}(C_{0.p}Z_{0.p}Z_{p.n+1})\right]\alpha \quad . \; . \; . \quad (22)$$

and

$$Z_1=Z_{1.n+1}-\left[\sum_{p=1}^{p=n}\sum_{q=p+1}^{q=n+1}(C_{p.q}Z_{p.q}^2)+\sum_{p=2}^{p=n+1}(C_{0.p}Z_{0.p}Z_{1.p})\right]\alpha, \quad . \; . \; . \quad (23)$$

where $Z_0 i_0$ is the potential of the point 1 below earth, and

$$i_0=i\left[1-\sum_{q=1}^{q=n+1}(Z_{0.q}C_{0.q})\alpha\right]. \quad . \; . \; . \; . \; . \quad (24)$$

Also, if i' be the current leaving the network,

$$i'/i=1-\sum_{q=0}^{q=n+1}(Z_{0.q}C_{0.q})\alpha. \quad . \; . \; . \; . \; . \; . \quad (25)$$

(*b*) *Formulæ for Residual Inductance.*

Besides intercapacities, the wires have a small self-inductance L per unit length, given by Rosa * :

$$L=2[\log(2l/r)-1+\mu/4], \quad . \; . \; . \; . \quad (26)$$

where l is the length of the wire, r its radius, μ the permeability of the wire, that of the dielectric being unity.

Also there are small mutual inductances M between the wires, given by *

$$M=\pm 2[\log(2l/d)-1+d/l], \quad . \; . \; . \; . \quad (27)$$

where d is the distance apart of the wires. The mutual inductance between the wires p and q, connected in the same sequence as in fig. 1, will be negative if $(q-p)$ is odd and positive if $(q-p)$ is even. In general, the last term of equation (27) can be neglected.

---

* "Self and Mutual Inductances of Linear Conductors," by E. B. Rosa, Bull. Bureau of Standards, vol. iv. p. 301 (1907).

It should be noticed that formulæ (4) and (5), (26) and (27) only hold for wires of circular cross-section.

Let us first assume that there are no capacities (which might be produced by terminals etc.) at the ends of the wires. Consider a point P_m on the wire m (fig. 1) distant x from m. Let Z_m, $M_{m.r}$, $K_{m.r}$, $K_{0.m}$ be the constants per unit length of this wire. Then

$$-\frac{di_{m+x}}{dx}=\sum_{r=0}^{r=n}(K_{m.r}V_{m+x.r+x})\,\alpha, \quad . \quad . \quad . \quad . \quad (28)$$

where i_{m+x} is the current at P_m and $V_{m+x.r+x}$ is the potential difference between P_m and P_r on the same level as P_m on the rth wire. Also

$$-\frac{dV_{m+x}}{dx}=i_{m+x}Z_m+\sum_{r=1}^{r=n}(M_{m.r}i_{r+x})\,\alpha. \quad . \quad . \quad (29)$$

Integrating equation (28) between the limits 0 and l, we have

$$i_m-i_{m+1}=\sum_{r=0}^{r=n}\left\{K_{m.r}li_1\left[Z_{m.r}+(Z_r-Z_m)\frac{l}{2}\right]\alpha\right\},$$

where $Z_{m.r}$ is negative if $r<m$, and *vice versa*, i_m and i_{m+1} being the currents at the points m and $(m+1)$ respectively.

By taking the sum of this between 1 and $(m-1)$, we shall have an equation connecting i_m and i_1, by which i_m can be eliminated in the expression obtained on integrating equation (29). On rearranging, we finally have the impedances Y_0, Y_1 of the whole given by the general expressions :—

$$\begin{aligned}Y_0&=\sum_{m=1}^{m=n}(V_m/i_0)\\&=Z_{1.n+1}+\Bigg[\sum_{m=1}^{m=n}\sum_{r=1}^{r=n}(M_{m.r}l)-\sum_{m=1}^{m=n}\sum_{r=m+1}^{r=n}(K_{m.r}lA_{m.r})\\&\qquad+\sum_{m=1}^{m=n}\left\{K_{0.m}l\left[Z_{0.m}Z_{m+1.n+1}+Z_ml\left(\tfrac{1}{2}Z_{0.n+1}-\tfrac{1}{3}Z_ml\right)\right]\right\}\Bigg]\alpha,\end{aligned}$$

$$. \quad . \quad . \quad (30\text{ A})$$

and

$$\begin{aligned}Y_1&=Z_{1.n+1}+\Bigg[\sum_{m=1}^{m=n}\sum_{r=1}^{r=n}(M_{m,r}l)-\sum_{m=1}^{m=n}\sum_{r=m+1}^{r=n}(K_{m.r}lA_{m.r})\\&\qquad-\sum_{m=1}^{m=n}\left\{K_{0.m}l\left[Z_{0.m}Z_{1.m+1}-Z_ml\left(\tfrac{1}{2}Z_{0.1}-\tfrac{1}{3}Z_ml\right)\right]\right\}\Bigg]\alpha,\end{aligned}$$

$$. \quad . \quad . \quad (30\text{ B})$$

where

$$A_{m.r} = Z_{m+1.r+1}\left[Z_{m.r} + (Z_r - Z_m)\frac{l}{2}\right] + \frac{Z_{m.r}}{2}(Z_m - Z_r)\,l$$
$$-(Z_m - Z_r)^2\frac{l^2}{6} \quad \text{if } (r-m) \text{ is even,}$$

and

$$A_{m.r} = Z_{m+1.r+1}\left[Z_{m.r} + (Z_r - Z_m)\frac{l}{2}\right] + \frac{Z_{m.r}}{2}(Z_m - Z_r)\,l$$
$$-(Z_m - Z_r)^2\frac{l^2}{6} + \frac{1}{3}Z_m Z_r l^2 \quad \text{if } (r-m) \text{ is odd.}$$

Three special cases will be considered :—

(i.) If all the wires are equal and have a resistance R each, we have

$$Y_0 = nR + \Bigg[L_{1.n+1} + 2\sum_{m=1}^{m=n}\sum_{r=m+1}^{r=n} M_{m.r}\,l - \sum_{m=1}^{m=n}\sum_{r=m+1}^{r=n} R^2(K_{m.r}\,l A_{m.r})$$
$$+\sum_{m=1}^{m=n}\Bigg\{K_{0.m}\,l\Bigg[Z_{0.1}R(n-m+\tfrac{1}{2})$$
$$+R^2\left(\{n-m+1\}m - \frac{n}{2} - \frac{1}{3}\right)\Bigg]\Bigg\}\Bigg]\alpha, \quad . \quad . \quad . \quad . \quad (31)$$

where

$$A_{m.r} = (r-m)^2 + \tfrac{1}{3} \quad \text{if } (r-m) \text{ is odd}$$

and

$$A_{m.r} = (r-m)^2 \quad \text{if } (r-m) \text{ is even.}$$

In the equation for Y_1 the last term is

$$-\sum_{m=1}^{m=n}\left\{K_{0.m}\,l\left[Z_{0.1}R(m-\tfrac{1}{2}) + R^2(m^2 - m + \tfrac{1}{3})\right]\right\}\alpha.$$

(ii.) If the wires are all equally spaced, equation (31) can be written in the form :

$$Y_0 = nR + l\Bigg[2\log\left\{\frac{(2l)^\gamma}{r^n}\right\}$$
$$+4\sum_{m=2}^{m=n}\left\{(-1)^m(n-m+1)\left(\log d_{1.m} - \frac{d_{1.m}}{l}\right)\right.$$
$$+2\left(\frac{n\mu}{4} - \gamma\right) - \sum_{m=1}^{m=n}\Bigg\{(n-m+1)R^2K_{1.m}A_{1.m}$$
$$-K_{0.m}\left[Z_{0.1}R(n-m+\tfrac{1}{2}) + R^2\left(\{n-m+1\}m - \frac{n}{2} - \frac{1}{3}\right)\right]\Bigg\}\Bigg]\alpha,$$
$$. \quad . \quad . \quad (32)$$

where $\gamma = 0$ if n is even (which is the usual case) and $\gamma = 1$

if n is odd; $A_{1.m}$ has the same value as in equation (31); $d_{1.r}$ is the distance between the 1st and the rth wire. The last term in the equation for Y_1 is the same as in case (i.).

(iii.) If $K_{0.m}$ has the same value (K_0, say) for all the wires, equation (32) can be further simplified. This will occur if all the wires are evenly spaced round the circumference of a cylinder concentric with the shield, or, again, if ρ in equation (15) is sufficiently small—that is, the distance between the wires and the shield is small compared with its radius. In the latter case, however, there must be no bodies within the shield other than the wires used. Thus it would not necessarily hold if only a few of the wires were used and the rest connected to the shield or left floating.

With these conditions, equation (32) becomes

$$\begin{aligned} Y_0 = nR + l\Big[& 2\log\left\{\frac{(2l)^\gamma}{r^n}\right\} \\ & + 4\sum_{m=2}^{m=n}\left\{(-1)^m(n-m+1)\left(\log d_{1.m} - \frac{d_{1.m}}{l}\right)\right\} \\ & + 2\left(\frac{n\mu}{4}-\gamma\right) - R^2\sum_{m=2}^{m=n}\left\{(n-m+1)K_{1.m}A_{1.m}\right\} \\ & + K_0\left(Z_{0.1}R\frac{n^2}{2} + R^2\frac{n^3}{6}\right)\Big]\alpha. \quad . \quad . \quad . \quad . \quad (33) \end{aligned}$$

The last term in the equation for Y_1 is

$$-K_0 l\left(Z_{0.1}R\frac{n^2}{2} + R^2\frac{n^3}{3}\right)\alpha.$$

To allow for the capacities $C_{m.r}$ between the terminals at the points m and r and the earth-capacities $C_{0.m}$, $C_{0.r}$ between the terminals and earth, we can use equations (22) and (23), for the whole resistance can be considered to be made up of impedances of value (V_m/i) in series interconnected with capacities.

Hence, the total impedance is given by

$$Z_0 = Y_0 - \left[\sum_{p=1}^{p=n}\sum_{q=p+1}^{q=n+1}(C_{p.q}Z_{p.q}^2) - \sum_{p=1}^{p=n}(C_{0.p}Z_{0.p}Z_{p.n+1})\right]\alpha \quad . \quad (34)$$

and

$$Z_1 = Y_1 - \left[\sum_{p=1}^{p=n}\sum_{q=p+1}^{q=n+1}(C_{p.q}Z_{p.q}^2) + \sum_{p=2}^{p=n+1}(C_{0.p}Z_{0.p}Z_{1.p})\right]\alpha. \quad . \quad (35)$$

(c) *Application to Bridges.*

When a high impedance is put in a bridge a difficulty is met at once in defining the meaning of impedance, for, owing to capacity currents, the current entering any specific part of the bridge may not equal the current leaving it. We shall consider as a typical case the simple four-arm bridge (fig. 2).

The condition for balance is

$$V_{AB}/V_{BC} = V_{DA}/V_{CD}.$$

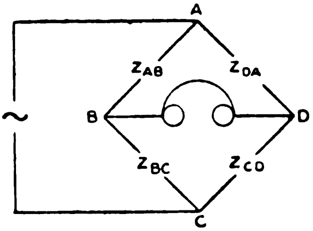
This can be written

$$(V_{AB} \cdot i_B)/(V_{BC} \cdot i_B) = (V_{DA} \cdot i_D)/(V_{CD} \cdot i_D)$$

or

$$Z_{AB}/Z_{BC} = Z_{DA}/Z_{CD}.$$

Fig. 2.



We see, therefore, that the impedance of any arm is defined as the ratio of the potential difference and the current at the end of the arm connected to the telephone.

Suppose the point *c* is earthed. The impedance will not include the earth capacity currents, so that we can use equation (22), in which $Z_{0.1} = Z_{BC}$ and B is taken as the point of the network to which the equation belongs. On the other hand, the impedance Z_{BC} will include the earth capacity currents, so that we must use equation (23) for it, putting $Z_{0.1} = -Z_{BC}$, where B is taken as the point 1.

If the telephone is earthed, we can consider that the earthing-wire is split in two on either side of B, so that the earth capacity current flows through B. The impedance of AB and BC is, therefore, given by equation (23), in which $Z_{0.1} = 0$ and B is taken as the point 1.

The last case of importance occurs when the telephone is kept at earth potential by means of a Wagner earth. In this case the earth capacity current does not flow through B and the impedance of AB and BC is given by equation (22), in which $Z_{0.1} = 0$ and B is taken as the point 1.

The same reasoning applies, of course, to the other two arms of the bridge CD and DA.

(d) *Case of a Single Loop.*

A special case of interest is that of two equal long parallel wires symmetrically situated with respect to the screen, with terminals at the end having capacities $C_{1.2}$ between them and $C_{0.1}$ to the screen. If R_0 is the total resistance of the two wires together, we have from equation (34)

$$Z_0 = R_0 + \left\{ 4l[\log(2a/r) + \tfrac{1}{4}] - R_0^2 \frac{l}{3} K_{1.2} \right.$$
$$\left. + R_0 l K_{0.1}\left(Z_{0.1} + \frac{R_0}{3}\right) + C_{0.1}(R_0 Z_{0.1} - C_{1.2} R_0^2) \right\} \alpha, \qquad (36)$$

where r is the radius of the wires and $2a$ their distance apart. When the radius R of the screen is infinite, $K_{0.1} = C_{0.1} = 0$ and the equation becomes

$$Z_0 = R_0 + \left\{ 4l[\log(2a/r) + \tfrac{1}{4}] - \frac{R_0^2 l}{12 \log(2a/r)} - R_0^2 C_{1.2} \right\}, \qquad (37)$$

which is the formula given by S. L. Brown *.

Let us consider how large the radius of the screen must be for this equation to hold.

If $Z_{0.1} = 0$—that is, one terminal is at earth potential—the last two terms in equation (35) become

$$-\frac{R_0^2 l}{6} \cdot \frac{\log\{(4\lambda^2+1)^2/\lambda/[4\lambda\mu(4\lambda^2-1)]\}}{\log\{\mu(4\lambda^2-1)/(4\lambda^2+1)\}\log\{\mu(16\lambda^4-1)/16\lambda^2\}}$$
$$- R_0^2 C_{1.2}, \quad . \quad . \quad . \qquad (38)$$

where $\lambda = R/d$ and $\mu = d/r$.

Also, if $Z_{0.1} = \frac{1}{2} R_0$—that is, the mid-point of the resistance is at earth potential—this becomes

$$-\frac{R_0^2 l}{12} \cdot \frac{1}{\log\{\mu(4\lambda^2-1)/(4l^2+1)\}} - R_0^2(C_{1.2} + \tfrac{1}{2} C_{0.1}). \qquad (39)$$

When λ is large, expression (39) is very nearly identical with the expression for an infinitely distant screen for the measured capacity between the terminals is $(C_{1.2} + \frac{1}{2} C_{0.1})$. The same is not true for expression (38).

TABLE II.

Coefficient of $R_0^2 l$ in expression (36), $Z_{0\cdot1} = 0$.

$\lambda =$	10	100	1000	10,000	
$\mu =$ 10	0	−0·0144	−0·020	−0·024	−0·036
= 100	0·0045	0	−0·0046	−0·0072	−0·018
= 1000	0·0096	0·0034	0	−0 0022	−0·012

In Table II. the value of the coefficient of $R_0^2 l$ of the first term of that expression is given for various values

---

* *L. c. ante.*

of λ and μ. It will be seen that, as μ will usually lie between 100 and 1000, this coefficient will require an enormous value of λ to approach its limiting value. Thus, if $\mu=100$ and $d=1$ cm., this coefficient only reaches half its limiting value when all objects connected to earth are removed to a distance of one kilometre.

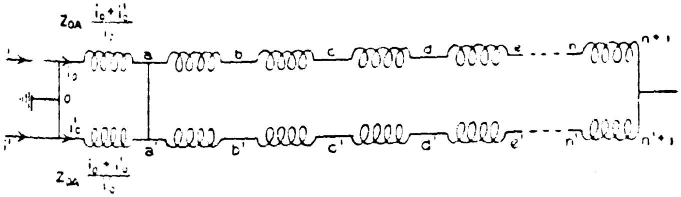
A similar result is obtained when Z_1 of equation (35) is taken instead of Z_0. Hence S. L. Brown's formula only applies when the mid-point of the resistance is at earth potential; but we saw in section III C. that in bridges $Z_{0.1}$ was either zero or positive, so that the conditions necessary for S. L. Brown's formula do not obtain. Experimental agreement was obtained because only differences were being measured, and the effect of the closeness of the earth would be substantially the same in both cases.

IV. STANDARD RATIO ARMS.

(a) *General Theorem for Two Impedances in parallel.*

Consider n impedances in parallel with n' impedances (n does not necessarily equal n') interconnected by capacities at all points between the impedances. Let Z_{0A} be the impedance between the point a and a' and 0, which is connected to earth. This impedance can be split up into two impedances in parallel, $Z_{0A}(i_0+i'_0)/i_0$ and $Z_{0.A}(i_0+i'_0)/i'_0$, carrying the currents i_0 and i'_0 respectively. (Fig. 3.)

Fig. 3.



Using the same notation as previously, we have

$$V_m = Z_m i_m,$$

and

$$i_0 = i_m + \sum_{p=a}^{p=m} \sum_{q=0}^{q=n+1} (C_{p.q}V_{p.q})\alpha + \sum_{p=a}^{p=m} \sum_{q=a'}^{q=n'+1} (C_{p.q}V_{p.q})\alpha \qquad (40)$$

and

$$i = i_m + \sum_{p=0}^{p=m} \sum_{q=0}^{q=n+1} (C_{p.q}V_{p.q})\alpha + \sum_{p=a}^{p=m} \sum_{q=a'}^{q=n'+1} (C_{p.q}V_{p.q})\alpha, \qquad (41)$$

and similarly for i'_0 and i'.

Now,
$$\sum_{m=0}^{m=n}(V_m)=\sum_{m=0}^{m=n'}(V_m).$$

Writing P_0 and P'_0 for the expressions of the impedances as given in section III. for each of the two networks in parallel (these experiments will, of course, not contain the terms involving the capacities or mutual inductances between one network and the other), we have

$$\frac{i_0}{i'_0}\equiv\frac{Z'_0}{Z_0}=\sigma\Bigg\{1+\Bigg[\frac{P'_0}{Z_{a'.n'+1}}-\frac{P_0}{Z_{a.n+1}}+\sum_{p=a}^{p=n+1}\sum_{q=a'}^{q=n'+1}C_{p,q}(Z_{p.n+1}+Z_{q.n'+1})\left(\frac{Z_{a'.q}}{Z_{a'.n'+1}}-\frac{Z_{a.p}}{Z_{a.n+1}}\right)\Bigg]\alpha\Bigg\}, \quad . \quad . \quad . \quad (42)$$

where $\sigma=Z_{a'.n'+1}/Z_{a.n+1}$ and Z_0, Z'_0 are the effective impedances of each of the two networks in parallel. P_0 and P_0' are given by equation (22), where $Z_{0.a}=Z_{0.A}\left(1+\frac{1}{\sigma}\right)$ and $Z_{0.a'}=Z_{0.A}(1+\sigma)$.

Also

$$\frac{i}{i'}\equiv\frac{Z_1'}{Z_1}=\sigma\Bigg\{1+\Bigg[\frac{P_1'}{Z_{a'.n'+1}}-\frac{P_1}{Z_{a.n+1}}+\sum_{p=a}^{p=n+1}\sum_{q=a'}^{q=n'+1}C_{p.q}(Z_{p.n+1}+Z_{q.n'+1})\left(\frac{Z_{a'.q}}{Z_{a'.n'+1}}-\frac{Z_{a.p}}{Z_{a.n+1}}\right)\Bigg]\alpha\Bigg\}, \quad . \quad . \quad . \quad (43)$$

where P_1 and P_1' are given by equation (23).

P_0, P_0', Z_0, Z_0' of equation (42) are the same as P_1, P_1', Z_1, Z_1' of equation (43), except that the former refer the impedances to the current entering the network including the earth capacity current, while the latter refer to the current entering the network excluding the earth capacity current.

(b) *Formulæ for Ratio.*

We shall now apply the last result to the calculation of the true ratio of the standard used as ratio arms.

As before, we shall assume at first that there are no capacities at the ends of the wires. Consider a point P_m on the wire m (fig. 1) distant x from m. With the same notation as before, we have

$$-\frac{di_{m+x}}{dx}=\sum_{r=0}^{r=n}(K_{m.r}V_{m+x.r+x})\alpha+\sum_{r=a'}^{r=n'}(K_{m.r}V_{m+x.r+x})\alpha \quad . \quad (44)$$

and

$$-\frac{dV_{m+x}}{dx}=i_{m+x}Z_m+\sum_{r=a}^{r=n}(M_{m.r}i_{r+x})\alpha+\sum_{r=a'}^{r=n'}(M_{m.r}i_{r+x})\alpha, \quad (45)$$

where $M_{m.r}$ is given by equation (27). It should be noticed that, if the current enters the two arms at the same end, the mutual inductance between one wire m in one arm and one wire r in the other is negative if $(r-m)$ is odd and positive if $(r-m)$ is even.

To make the conditions more general, we shall assume the arms to be connected in series with external impedances Z_{Aa} and $Z_{Aa'}$, the standard containing n and n' wires respectively numbered from a to n and a' to n'.

These external impedances will be assumed to have zero mutual inductance with the standard, and there will, of course, be no capacity between them and the standard, since the latter is completely screened.

From equations (44) and (45), by integrating between the limits 0 and l and neglecting small terms of the second order, we obtain a general expression for $(Z_{A.n'+1}/Z_{A.n+1})$. The complete expression is lengthy, and, as the only case of importance is that when all the wires are equal and of resistance R, the simplified results in these conditions are given by

$$\frac{Z_{A.n'+1}}{Z_{A.n+1}}=\frac{Z_{A.a'}+Q'}{Z_{A.a}+Q}\left[1+R^2\sum_{p=a}^{p=n}\sum_{q=a'}^{q=n'}\left\{K_{p.q}l\left(\frac{B'_{p.q}}{Z_{A.a'}+Q'}-\frac{B_{p.q}}{Z_{A.a}+Q}\right)\alpha\right\}\right.$$
$$\left.+\left(\frac{1}{Z_{A.a'+Q'}}-\frac{1}{Z_{A.a+Q}}\right)\sum_{p=a}^{p=n}\sum_{q=a'}^{q=n'}(M_{p.q}\alpha)\right], \quad . \quad . \quad (46)$$

where Q and Q′ are the expressions of the impedances as given in equations (31), (32), and (33) for each of the two radio arms of the standard, and

$$\begin{aligned} B'_{p.q} &= (n'-q)(q-\tfrac{1}{2})+q-\tfrac{1}{2} \text{ if } q-p \text{ is odd,} \\ &= (n'-q)(q-\tfrac{1}{2})+q-\tfrac{2}{3} \text{ if } q-p \text{ is even,} \\ \text{and} \quad B_{p.q} &= (n-p)(p-\tfrac{1}{2})+p-\tfrac{1}{2} \text{ if } q-p \text{ is odd,} \\ &= (n-p)(p-\tfrac{1}{2})+p-\tfrac{2}{3} \text{ if } q-p \text{ is even.} \end{aligned}$$

To allow for the capacities between the terminals at the ends of the wires, we can now use equations (42) and (43), in which we substitute $(Z_{A.n'+1}/Z_{A.n+1})$ as given in equation (46) for σ.

(c) *Application to Bridges.*

The same arguments can be applied regarding the application of ratio arms in bridges as was used when a non-inductive resistance was considered. Let AB and AD (fig. 2) be the ratio arms. Four cases arise :

(1) When C is earthed, the impedances Z_{AB} and Z_{AD} will not include the earth capacity currents, so that equation (42) will apply. The points B and D (which are electrically the same when balance is obtained) will correspond to the point *a* of the ratio arms and $Z_{0a}=Z_{BC}$ and $Z_{0a'}=Z_{DC}$.

(2) When A is earthed, the earth capacity currents will be included in the impedances Z_{AB} and Z_{AD}, so that equation (43) will now hold. The points B and D will, as before, correspond to the point *a* of the ratio arms, and we must put $Z_{0.a}=-Z_{AB}$ and $Z_{0.a'}=-Z_{AD}$.

(3) When the telephone is earthed at B or D, the earth capacity currents will be included and equation (43) must be used. The points B and D will correspond to the point *a* of the ratio arms and $Z_{0.a}=Z_{0.a'}=0$.

(4) When the telephone is kept at earth potential by a Wagner earth, equation (42) will hold. The points B and D will correspond to the point *a* of the ratio arms and $Z_{0.a}=Z_{0.a'}=0$.

V. STANDARD POTENTIAL DIVIDER.

(a) *General Formulæ.*

In this case we require to find the ratio of the voltage between any two points *r* and *s* and the total voltage across the resistance. It will be supposed that no current is taken at the points *r* and *s*, but the capacity of the leads etc. connected to those two points must be taken into account in the usual way.

From equation (20) we have

$$\frac{V_{r.s}}{i_0}=\sum_{m=r}^{m=s-1}(V_m/i_0)$$

$$=Z_{r.s}\left[Z_{r.s}\sum_{p=1}^{p=r}\sum_{q=0}^{q=n+1}(C_{p.q}Z_{p.q})+\sum_{p=r+1}^{p=s-1}\sum_{q=0}^{q=n+1}(C_{p.q}Z_{p.q}Z_{p.s})\right]\alpha, \quad . \quad . \quad . \quad (47)$$

giving the potential difference between the points *r* and *s* when the potential divider is assumed to be made up of *n* impedances in series.

By putting $r=1$ and $s=n+1$, we obtain the potenti difference across the whole. From this, we have

$$\frac{V_{r.s}}{V_{1.n+1}}=\frac{Z_{r.s}}{Z_{1.n+1}}\left\{1-\left[\sum_{p=2}^{p=r}\sum_{q=0}^{q=n+1}(C_{p.q}+Z_{p.q})\right.\right.$$

$$+\frac{1}{Z_{r.s}}\sum_{p=r+1}^{p=s-1}\sum_{q=0}^{q=n+1}(C_{p.q}Z_{p.q}Z_{p.s})$$

$$\left.\left.-\frac{1}{Z_{1.n+1}}\sum_{p=2}^{p=n}\sum_{q=0}^{q=n+1}(C_{p.q}Z_{p.q}Z_{p.n+1})\right]\alpha\right\}. \quad (48)$$

Now suppose the tapping points are at points distant x and y from r and s respectively. Let us call these points $(r+x)$ and $(s+y)$.

From equations (28) and (29) it can be shown that

$$\frac{V_{r+x.s+y}}{i_1}=Z_{r+x.s+y}+\left[\sum_{p=1}^{p=n}\left\{M_{s.p}y-M_{r.p}x+\sum_{q=r}^{q=s-1}(M_{p.q}l)\right\}\right.$$

$$-\sum_{p=r-1}^{p=s-1}\sum_{q=p+1}^{q=n}(K_{p.q}lA_{p.q})$$

$$-\sum_{p=1}^{p=r-1}K_{0.p}l\left\{Z_{0.p}Z_{p+1.r}+Z_{p}l\left(\frac{1}{2}Z_{0.r}-Z_{p}\frac{l}{3}\right)\right\}$$

$$-Z_{r}x\sum_{p=0}^{p=n}(\tfrac{1}{2}K_{rp}xB_{r.p})$$

$$+\sum_{p=1}^{p=s-1}K_{0.p}l\left\{Z_{0.p}Z_{p+1.s}+Z_{p}l\left(\frac{1}{2}Z_{0.s}-Z_{p}\frac{l}{3}\right)\right\}$$

$$+Z_{s}y\sum_{p=0}^{p=n}(\tfrac{1}{2}K_{s.p}yB_{s.p}), \quad . \;.\; . \quad (49)$$

where

$$A_{p.q}=\left[Z_{p.q}+(Z_{q}-Z_{p})\frac{l}{2}\right]Z_{p+1.q+1}+\tfrac{1}{2}Z_{p.q}(Z_{p}-Z_{q})l$$

$$-\frac{l^{2}}{6}(Z_{p}-Z_{q})^{2} \quad \text{if } (q-p) \text{ is even,}$$

and

$$A_{p.q}=\left[Z_{p.q}+(Z_{q}-Z_{p})\frac{l}{2}\right]Z_{p+1.q+1}+\tfrac{1}{2}Z_{p.q}(Z_{p}-Z_{q})l$$

$$-\frac{l^{2}}{6}(Z_{p}+Z_{q})^{2}+Z_{p}Z_{q}l^{2} \quad \text{if } (q-p) \text{ is odd.}$$

Also

$$B_{r.p}=Z_{r.p}+(Z_p-Z_r)\frac{x}{3} \quad \text{if } (p-r) \text{ is even,}$$

and

$$B_{r.p}=Z_{r.p+1}-(Z_p+Z_r)\frac{x}{3} \quad \text{if } (p-r) \text{ is odd.}$$

(For $B_{s.p}$ put y instead of x and s instead of r.)

The general expression for $(V_{1.n+1}/i_1)$ is given by equation (30 B) By dividing equation (49) by this, we obtain the ratio $(V_{r+x.s+y}/V_{1.n+1})$.

To allow for the capacities of the terminals, this ratio must be substituted for $(Z_{r.s}/Z_{1.n+1})$ in equation (48).

This may appear very laborious, but at the worst when there are many wires it only involves very simple arithmetic. The expression $(V_{r+x.s+y}/i_1)$ is usually simplified by the fact that all the wires will in general be of the same resistance R, and very often the earth capacity terms will be large compared with the other capacity terms. Besides this, in the usual case, $r=1$ and $x=y=0$.

When all the wires are of resistance R, the values of $A_{p.q}$ and $B_{p.q}$ simplify to

$$A_{p.q} = [(q-p)^2+\tfrac{1}{3}]R^2 \quad \text{if } (p-q) \text{ is odd,}$$

and

$$A_{p.q} = (q-p)^2R^2 \quad \text{if } (p-q) \text{ is even.}$$

Also

$$B_{r.p} = \left(p-r+\frac{x}{3}\right)R \quad \text{if } (p-r) \text{ is odd,}$$

and

$$B_{r.p} = (p-r)\,R \quad \text{if } (p-r) \text{ is even.}$$

(b) *Application.*

Apart from the general use of the potential divider at audio and radio frequencies, the standard may be of special use for obtaining small known voltages at radio frequencies, the voltage across the whole resistance being measured by an electrostatic voltmeter. When very low voltages are required, it would be easier to connect a low variable resistance in series with the standard and take off the desired voltage across that resistance. It is, of course, assumed that the frequency is never so high that terms containing squares of the capacities cannot be neglected.

We have seen that, to obtain a calculable solution, it was necessary to have the shield fairly close to the wires. When dealing with very high voltages, this may bring a difficulty of corona effects and sparking directly to the screen. If a number of standards are used in series this might largely be obviated by connecting the screen to one of its terminals, so that the potential difference in any one of them is only a fraction of the total. It will then become necessary to measure or calculate the capacity of the various screens to earth. For calculation, the simplest case would be to place all the standards in a line and surround the whole with a concentric metal shield (which can be a simple wire mesh), when capacity of each standard to earth will be

$$\frac{l}{2\log(r_1/r_2)},$$

where r_1 and r_2 are the radii of the external screen and of the standard respectively, l being the length.

VI. General Construction.

(a) *Design.*

The case of a 10,000 ohm standard will be considered. If No. 47 manganin wire, radius 0·0025 cm., is used, it may consist of 40 wires about 106 cm. long. The angle subtended at the centre by two consecutive wires will thus be 9°. From Table I. it must therefore be of the order of 0·1 or less. Suitable values are :

Internal radius of screen . . = 2 inches.
Distance of wires from centre = 1·8 „

Hence

$$\rho = 0{\cdot}111.$$

If there are no lumped capacities at the terminals, the total impedances of the 40 wires in series will be, from equation (33),

$$Y_0 = 10{,}000 + {\cdot}00935\alpha$$

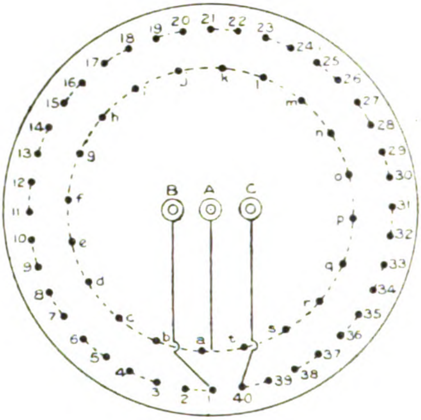
and

$$Y_1 = 10{,}000 - {\cdot}0201\alpha.$$

To allow this standard to be used for a number of values of resistance, the wires must be connected to terminals at one end ; at the other end they would simply be held taut by springs, to which they would not be electrically connected. In order to keep the wires in position along their whole length, they could be supported at intervals by ebonite bridges.

A suitable arrangement of the terminals is shown in fig. 4. The large dots represent the terminals (which may take the form of a split wire) to which the wires are fixed. The resistance wires 1 and 2, 3 and 4, etc., are connected at the further end, and the wires 2 and 3, 4 and 5, etc., can be connected by thin copper wires at the terminals. The other circle of terminals are all connected together by a thin copper wire and serves as a connecting-link between the last wire and terminal A.

Fig. 4.



Thus, if terminal 10 is connected to *e*, the resistance will be 2500 ohms. All the other wires will be connected together and to earth. In such a case the values of the capacities to earth will be slightly altered, because of the other earthed wires and terminals. The capacity to earth of any wire will be its usual value plus the sum of the capacities between the wire under consideration and all the earthed wires.

The correction due to the return path *a*, *b*, *c*, *d*, *e*, ... can be allowed for, if the capacities are known and the mutual inductance is negligible.

Three terminals ABC are shown to allow for the standard to be used as ratio arms, one arm starting at wire 1 and the other at wire 40. In this case it would be advisable to cut the return wire *a*, *b*, *c* ... at some point in between the two arms.

The measurement of the terminal capacities will be somewhat lengthy, owing to their large number. Fortunately, the work is considerably shortened owing to the symmetry of the arrangement. It is necessary to know the capacity of any terminal to the screen, to any other terminal, and to the return wire.

Connect all the wires except the *m*th and *r*th together. Call this A and the screen S. By connecting *m*, *r*, S, and A in various ways we can find their capacity thus.

Connecting A and *r* to S and finding the capacity to *m*, we have

$$C_{Am}+C_{mr}+C_{mS} = C_1.$$

Connecting *r* to S and A to *m* and finding the capacity between them, we have

$$C_{Ar}+C_{AS}+C_{mS}+C_{mr} = C_2.$$

Connecting *m* and *r* to S and finding the capacity to A, we have

$$C_{AS}+C_{Am}+C_{Ar} = C_3.$$

Connecting A to S and *m* to *r* and finding the capacity between them, we have

$$C_{m.S}+C_{r.S}+C_{A.m}+C_{A.r} = C_4.$$

Therefore, since *m* and *r* are symmetrical,

$$\begin{aligned} C_{A.r} = C_{A.m} &= \tfrac{1}{2}(C_1+C_3-C_2), \\ C_{A.S} &= C_2-C_1, \\ C_{r.S} = C_{m.S} &= \tfrac{1}{2}(C_4+C_2-C_1-C_3), \\ C_{m.r} &= C_1-\tfrac{1}{2}C_4. \end{aligned}$$

The value of C_1 must be found for all values of *r*. From this, since C_4 is from symmetry independent of *r*, we can find the values of $C_{m.r}$ for all values of *r*, and, since

$$C_{m.S} = C_{0.m}+\sum_{p=1}^{p=n}(C_{m.p})-C_{m.r},$$

where $C_{0.m}$ is the capacity to the screen alone, we can find $C_{0.m}$.

The intercapacities and capacities to earth of the terminals A, B, and C will have to be found in a similar way.

It will be seen that the capacities of the wires can be measured instead of calculated, when the wires are not permanently connected together. When this is done, the limitation of having to screen close to the wire vanishes.

(b) *Accuracy.*

The intercapacities of the terminal can be measured by the method of L. Hartshorn *, by which these small capacities can be measured to within $0{\cdot}02\mu\mu F$. The error in the residual inductance due to this will, in a 10,000 ohm standard, be of the order of 005α.

---

* Proc. Phys. Soc. vol. xxxvi. p. 399 (1924).

The main term of the residual inductance is due to the earth capacities $K_{0.m}$, the other terms being but a few per cent. of this one. If errors of 10 per cent. occur in measuring the radius of the wires and the distance of the wires from the shield, the error in $K_{0.m}$ will be, for the case under consideration, of the order of 10 per cent. for the worst case, when all the errors are cumulative. Hence the maximum possible error in calculating the residual inductance of the standard, taking the error due to assumption of the wire being infinitely long into account, is about 11 per cent.

The accuracy of calculation depends largely on the accuracy of the measurement of the radius of the wire and of the distance between the wire and the shield, each representing a possible error of about 5 per cent. in the residual inductance for the case considered. To reduce the quadrature component, it would be necessary to use a larger shield and obtain $K_{0.m}$, $K_{m.r}$ by measurement.

January 13, 1926.

VI. *Atomic Structure and the Magnetic Properties of Coordination Compounds.* By L. C. JACKSON, *M.Sc., Ph.D., A.Inst.P., "1851 Exhibition" Senior Student* *.

THE magnetic properties of the coordination compounds of the elements between chromium and copper and their possible interpretation in terms of atomic structure have been discussed by a number of writers recently. Most of the authors take as their basis the scheme for the distribution of the electrons among the sub-groups of the various atomic levels put forward independently by Stoner † and Main-Smith ‡ for the case of normal atoms and the ions of simple salts. The proposed distributions of the electrons in and around the coordinating atoms differ, however, considerably in detail, and it is proposed here to discuss the various schemes put forward and to endeavour to show which is the most probable.

Our knowledge of the magnetic properties of coordination compounds is derived from the determinations of Oxley §,

---

* Communicated by the Author.

† Phil. Mag. xlviii. p. 714 (1924).

‡ 'Chemistry and Atomic Structure,' London, 1924.

§ Proc. Camb. Phil. Soc. xvi. p. 102 (1910-12).

Rosenbohm [*], and Welo [†]. Oxley has shown that potassium ferrocyanide is diamagnetic but that potassium ferricyanide is paramagnetic, the ferric atom possessing approximately ten Weiss magnetons. In these cases the properties of the metallic atom are very different from those possessed by that particular atom in simple salts.

Rosenbohm [‡] has determined the properties of a large number of complex ammines of chromium, cobalt, nickel and copper, together with those of platinum, iridium, ruthenium, and rhodium. We will confine ourselves here to the first group of compounds. Rosenbohm found that the sixfold compounds of chromium (Cr^{+++}) and nickel (Ni^{++}) were paramagnetic and possessed the same number of magnetons as these elements do in their simple salts, *i. e.*, approximately 19 and 16 respectively. A fourfold compound of nickel was also found to be paramagnetic, but to contain approximately 13 magnetons. The fourfold compounds of copper (Cu^{++}) were shown to be paramagnetic, with a magneton number somewhat smaller than that of the cupric ion in simple salts. The compounds of cobalt were found to be diamagnetic.

Rosenbohm's data, as Cabrera [§] has observed, require correction, firstly, because he made use of the value $-0{\cdot}75 \times 10^{-6}$ for the susceptibility of water instead of the now accepted value $-0{\cdot}719 \times 10^{-6}$, and secondly, because he did not apply any correction for the diamagnetic properties of the atoms or groups surrounding the central coordinating atom. These corrections are both relatively small and are of opposite sign, so that the corrected values do not differ greatly from Rosenbohm's original figures. Any of his data quoted in this paper have been corrected as mentioned above.

Welo [‖] has recently determined the magnetic properties of a number of complex ferro- and ferricyanides. He found that, with one doubtful exception [¶], all the ferrocyanides were diamagnetic. The ferricyanides were, however, paramagnetic and all contained approximately 10 magnetons.

---

[*] *Zeit. für Phys. Chem.* xciii. p. 693 (1919).

[†] 'Nature,' cxvi. p. 359 (1925).

[‡] The magnetic properties of a few of the coordination compounds have also been measured by Mlle. Feytis (*C. R.* clii. p. 708 (1911)). In some cases the results agree with those of Rosenbohm, but in others there are considerable discrepancies. Rosenbohm believes, in all probability correctly, that his data are the more trustworthy on account of the very special care he took to obtain absolutely pure compounds and to ensure the reproducibility of the results.

[§] *J. de Phys. et le Radium*, iii. p. 443 (1922).

[‖] *Loc. cit.*

[¶] See Welo and Baudisch, 'Nature,' cxvi. p. 606 (1925).

These experimental results have been discussed recently by Welo and Baudisch *, Bose †, and Cabrera ‡.

Starting from Sidgwick's § ideas as to the number of electrons transferred to or shared with the central coordinating atom, Welo and Baudisch calculate the total number of electrons associated with the central atom ‖. They thus obtain the following numbers for the elements mentioned (= atomic number + net number of electrons transferred or shared), $Cr^{+++}=33$, $Fe^{+++}=35$, $Fe^{++}=36$, $Co^{+++}=36$, Ni^{++} (sixfold) $=38$, (fourfold) $=34$, $Cu^{++}=35$.

The value 36 corresponds to the atomic number of argon, the next higher rare gas. The structure of the central atom when the "effective atomic number" is equal to 36 is then taken to be similar of that of argon. It would thus be expected that these compounds would be diamagnetic, as is actually the case.

Those compounds for which the "effective atomic number" is not equal to 36 are paramagnetic. Welo and Baudisch, in these cases, distribute the electrons among the various possible atomic levels in such a way as to lead to the observed magneton numbers. For the case of Fe^{+++}, in which 9 additional electrons are to be disposed of, they assign 5 of the 9 to the N level making it complete with 8 (actually only the N_{11}, N_{21}, and N_{22} sub-groups have then been completed), and assign the remaining 4 to the M level. There are then 17 electrons in this level, as there are in this level for the divalent copper ion. Since this ion possesses about 10 Weiss magnetons, the authors say that it is therefore to be expected that the ferricyanides would possess the same number. This is actually the case.

By assigning 5 of the available electrons to the N level of the chromium atom in the complex salts and 4 to the M level, this atom is made to simulate the structure of the divalent cobalt ion in its simple salts. Experimentally divalent cobalt gives a magneton number of about 24–25, which does not agree with the value 19 found in the complex chromium compounds. Welo and Baudisch, however, state that cobalt is anomalous and quote Sommerfeld's 1923

---

* *Loc. cit.*

† *Zeit. für Phys.* xxxv. p. 219 (1925); 'Nature,' cxvii. p. 84 (1926).

‡ *J. de Phys. et le Radium*, vi. p. 276 (1925).

§ Trans. Chem. Soc. cxxiii. p. 725 (1923).

‖ We shall confine the discussion here to those compounds with only one central metallic atom.

paper [*] as showing that a value 19·2 is expected for this ion. This argument does not seem very convincing, especially as the paper quoted has been superseded by later work [†], and the divalent cobalt ion can hardly be considered as being in an '*s*' state.

For the sixfold nickel compounds, for which there are 10 disposable electrons, the central nucleus is supposed to be similar to the strontium atom with atomic number 38. This is presumed to contain 2 Bohr magnetons or 14·1 Weiss magnetons. Again the agreement is not striking.

With the fourfold copper compounds, 6 electrons are to be added. These are supposed to complete the N level (actually the first three sub-groups) leaving the M level as in the simple divalent copper ion, and hence the Weiss magneton number also the same. Actually the magneton number for the coordination compounds of Cu^{++} is somewhat less than that of the Cu^{++} ion in simple salts, 9 instead of about 9·7.

Welo and Baudisch's treatment of the paramagnetic coordination compounds is thus not particularly successful, and it may be noted that a satisfactory account of the magnetic properties of atoms cannot be given without considering the distribution of the electrons among the sub-groups of the various levels. Atoms or ions containing the same total number of electrons in the various levels may have different magnetic properties if the distributions among the sub groups of the levels are different.

The objection may be raised to the scheme proposed by Welo and Baudisch that it does not bring out the character of the combination. The electron distribution does not show any evidence of the coordination numbers 6 or 4. The same objection may be made to the scheme proposed by Bose now to be discussed. An arrangement of the outer electrons corresponding to the known facts of the structure of these compounds has been proposed and discussed by Fowler [‡]. It will be shown later how the magnetic properties can be interpreted in terms of these ideas.

Bose in his treatment of the problem also defines the "effective atomic number" in a way which, though different in principle, arrives at the same results as that of Sidgwick. He then distributes the electrons among the various possible atomic levels in a way rather similar to that of Welo and Baudisch. He then states that the magneton number of any of these coordination compounds, expressed in Bohr magnetons, can be calculated from the following formula :—$Z-Z'=n$, in which Z=atomic number of next rare gas, in this case A=36, Z'="effective atomic number" of central coordinating atom, n=number of Bohr magnetons. The numbers so obtained are as follows :—Cr^{+++}=3, Fe^{+++}=1, Fe^{++}=0, Co^{+++}=0, Ni^{++} (sixfold) =2, Ni^{++} (fourfold) =2, Cu^{++}=1.

---

[*] *Zeit. f. Phys.* xix. p. 226 (1923).

[†] *Atombau u Spektrallinien*, 4te Auflage, p. 630.

[‡] Trans. Farad. Soc. xix. p. 102 (1923).

The electron distributions proposed by Bose are given in Table I.

TABLE I.

Ion.	Kind of compound.	No. of electrons.							Total no. of electrons.		Diff-erence.	Coord. no.
		M		N			O		imple ion.	Coord. atom.		
		32	33	11	21	22	11	21				
Cr^{+++}	simple ...		3						21		12	6
	complex...	4	3	2	2	4				33		
Fe^{+++}	simple ...		4	1					23		12	6
	complex...	4	6	1	2	4				35		
Fe^{++}	simple ...		4	2					24		12	6
	complex ..	4	6	2	2	4				36		
Co^{+++}	simple ...	2	4						24		12	6
	complex...	4	6	2	2	4				36		
Ni^{++}	simple ...	2	6						26			
	complex...	2	6	2	2	4				34	8	4
	complex...	2	6	2	2	4	2	2		38	12	6
Cu^{++}	simple ...	2	6	1					27		8	4
	complex...	4	6	1	2	4				35		

Such a rule as $Z-Z'=n$ does not seem likely to possess any definite physical meaning, containing as it does a number Z, which the coordinating atom may be said to strive to attain. In another paper* dealing with the distribution of the electrons among the M_{32} and M_{33} sub-groups for the normal atoms, and the ions of the simple salts of the elements of the first transition group, Bose has proposed the rule $M_{33}+N_{11}-M_{32}=n$, in which M_{33} etc. represent the number of electrons in the sub-group and n=number of Bohr magnetons. When, however, the sub-group is completed, the number of electrons in it count as zero, since it is generally accepted that the magnetic moment of a completed sub-group is zero. It would seem that an extension of this rule to the case of the coordination compounds would be physically more probable than the rule, $Z-Z'=n$, actually proposed.

It is easily seen that the obvious extension of the rule

$$M_{33}+N_{11}+N_{22}+O_{11}-M_{32}-N_{21}-O_{21}=n,$$

together with the same proviso when the sub-groups are completed, reproduces Bose's numbers just as well as his own rule. Even the new rule, however, can have no very profound meaning, since on inspecting the table, it is seen that either all the sub-groups are completed and so the total magnetic moment is zero, or all but one are completed and the moment of this one only comes into consideration.

The agreement between the calculated Bohr magneton numbers and the experimentally obtained Weiss magneton numbers is not satisfactory, but this is due rather to the present position of the quantum theory than to the particular ideas here discussed. To obtain the Weiss magneton numbers from the calculated Bohr values, Bose, similarly to Welo and Baudisch, makes use of the formula given by Sommerfeld in his 1923 paper. It would have been more in accord with the present state of the theory to have employed the later formula, $mg\sqrt{\frac{j+1}{j}}$, from which the magnetic moment for an atom in any particular state can be calculated. The old formula is equivalent to assuming that the atom in question is in an '*s*' state. With regard to the present position of the theory and in view of our complete ignorance of the spectra of the doubly and trebly ionized atoms of the elements from Cr to Cu, it is probably better not to attempt to calculate the magneton numbers corresponding to any particular distribution of electrons. One must at present rather be satisfied with showing that those atoms which have the same magnetic properties have the same structure and that this structure is in general agreement with known facts, in particular that the atoms of diamagnetic compounds have the various sub-groups completed.

---

* *Zeit. f. Phys.* xxxv. p. 215 (1925).

In his discussion of the magnetic properties of the coordination compounds, Cabrera has made use of the scheme put forward by Fowler. In this latter the electrons outside the K and L levels of a sixfold coordinating atom are supposed to tend to be distributed in the following groups :—8+6+12. The first 8 electrons are those occupying the M_{11}, M_{21}, and M_{22} sub-groups of the atom, the next 6 tend to collect into the M_{33} sub-group, and remaining 12 electrons are shared by the central atom and the groups surrounding it. These electrons are made up of those contributed by the various groups (their number can be calculated from Sidgwick's rules) together with the valency electrons of the central atom, *e. g.* in Fe^{++} 10+2, in Cr^{+++} 9+3. These electrons are probably arranged in 6 pairs of orbits and associated with the corners of a regular octahedron in agreement with the symmetry of the compounds according to Werner. This group of 12 electrons as a whole possesses no magnetic moment.

We thus have a very definite picture of the molecule, of the nature of the coordination number 6, and of the chemical bounds involved. The scheme thus possesses obvious advantages over schemes which involve distributing the "extra" electrons among the various atomic levels so as to make the central atom simulate the structure of some higher atom. As Fowler has pointed out, although the additional electrons might in certain compounds possibly be arranged in shells about the central atom somewhat as in a normal atom of higher atomic number, the orbits occupied by these electrons cannot be considered in the coordination compounds as in reality the same as the N_{11}, N_{21}, etc. orbits of a normal atom. Hence for this reason and because the schemes proposed by Welo and Baudisch and by Bose give no idea of the valency of the central coordinating atom nor of the coordination number of the compound, the scheme just discussed must be regarded as the most probable one.

We will now turn our attention to the ideas put forward by Cabrera to explain the magnetic properties of the coordination compounds. The distribution of the electrons in the ions of the simple salts of the elements from Cr to Cu as proposed by Cabrera in accordance with the ideas of Stoner and Main-Smith is as follows :—

TABLE II.

Ion.	No. of electrons.				
	M_{11}.	M_{21}.	M_{22}.	M_{32}.	M_{33}.
Cr^{+++}	2	2	4	-	3
Fe^{+++} Mn^{++}......	2	2	4	1	4
Co^{+++} Fe^{++}......	2	2	4	2	4
Co^{++}......	2	2	4	2	5
Ni^{++}......	2	2	4	2	6
Cu^{++}......	2	2	4	4	5

This scheme is in agreement with the known magnetic properties of the simple salts of these elements, but the distributions must not be regarded as fixed with certainty.

For the distribution of the electrons in the ions of the sixfold coordination compounds Cabrera proposes the following scheme :—

TABLE III.

Ion.	No. of electrons.					Binding electrons.
	M_{11}.	M_{21}.	M_{22}.	M_{32}.	M_{33}.	
Cr^{+++}	2	2	4	-	3	12
Co^{+++} Fe^{++} ...	2	2	4	-	6	12
Ni^{++}...	2	2	4	2	6	12

We see here the tendency of the M_{33} sub-group to fill to completion at the expense of M_{32}. In the case of Cr^{+++} there are no electrons in the M_{32} sub-group, so that M_{33} remains incomplete and the ion has the same structure as the ion in simple salts. In Co^{+++} and Fe^{++}, however, two electrons pass from the M_{32} to the M_{33} sub-group, making it complete with 6 electrons. Since M_{33} is already complete in Ni^{++} no change takes place in this ion. On examining Table III. we see that it is to be expected that the sixfold coordination compounds of Cr^{+++} and Ni^{++} should have the same magneton numbers as the corresponding simple salts. This is actually the case. Again, the coordination compounds of Co^{+++} and Fe^{++} should be diamagnetic since M_{32} contains no electrons and M_{33} is complete. This also agrees with the facts.

Welo's determinations of the magnetic properties of the complex ferro- and ferricyanides had not been published when Cabrera's paper was written. It can, however, easily be seen that the scheme accounts for the properties of these compounds also. We may suppose that the M_{33} sub-group in the ferricyanides also tends to complete itself with 6 electrons. It can, however, only obtain 5, so that the distribution is as follows :—

Ion.	No. of electrons.					Binding electrons.
	M_{11}.	M_{21}.	M_{22}.	M_{32}.	M_{33}.	
Fe^{+++}	2	2	4	-	5	12

We should therefore expect these substances to be paramagnetic and to possess a magneton number equal to that of the simple cupric salts, since the structures of the ions are the same except for the M_{32} sub-group. Since the latter is unoccupied in the ferricyanides and complete in the cupric salts, the net result is the same for both. Actually both groups of compounds contain approximately 10 Weiss magnetons.

Cabrera has also discussed the magnetic properties of the fourfold coordination compounds of Ni^{++} and Cu^{++}, and proposes the following scheme for the electron distribution.

Nucleus.	No. of electrons.					Binding electrons.
	M_{11}.	M_{21}.	M_{22}.	M_{32}.	M_{33}.	
Ni^{++}	2	2	4	4	4	8
Cu^{++}	2	2	4	4	5	8

In the case of the fourfold coordination compounds there are 8 binding electrons or four pairs, which, following

Werner and Sidgwick, are to be considered as associated with points lying, not at the corners of a tetrahedron, but in a plane and occupying, in the case of compounds in which the four groups are all the same, the corners of a square. Cabrera, arguing from analogy with the sixfold compounds, supposes that the M_{32} sub-group, which when complete possesses 4 electrons, will for this reason and because of the fourfold arrangement of the outer binding electrons tend to be completed at the expense of M_{33}. He therefore supposes that Ni^{++} has 4 electrons in both M_{32} and M_{33} in place of 2 in M_{32} and 6 in M_{33} as in the simple nickel salts. Since Cu^{++} already possesses 4 electrons in the M_{32} sub-group, the structure of this ion is the same in the fourfold coordination compounds and the simple cupric salts.

While this scheme may be said to give a fair account of the properties of the copper compounds, the complex compounds having a magneton number of about 9 and the simple salts of about 9·7, it does not seem so successful in the case of the nickel compounds. It would seem reasonable to expect that the 4.4 arrangement of the electrons would give a greater magneton number than the 2 6 arrangement of the simple salts. Actually the magneton number of the fourfold nickel compounds is about 13, while that of the simple nickel salts is 16. Cabrera admits that there are difficulties in the way of any scheme such as that which he proposes but considers that any different one, which would be successful for Ni^{++}, would probably encounter equal difficulties with Cu^{++}.

It would seem to the writer that a possible method of explaining the properties of the fourfold compounds is as follows. It may be quite possible that there is not the tendency of the M_{32} sub-group to be completed, as suggested by Cabrera, for the following reasons. Any tendency which the outer binding electrons will have in causing the M_{32} electrons to assume the symmetry of the former will be less than is the case for the M_{32} in the sixfold compounds, because the M_{32} electrons are to a certain extent shielded by the outer M_{33} electrons. Furthermore, it is quite possible that the symmetry of the 4 M_{32} electron orbits, when the sub-group is complete, is different from that of the outer binding electrons which are in one plane, the former possibly possessing tetrahedral symmetry. If it is allowed that these factors will reduce any tendency for the M_{32} sub-group to complete itself in the fourfold compounds, it will be seen then that the distributions of the electrons in the M_{32} and M_{33} sub-groups will be the same in the coordination compounds and the simple salts.

Since, however, these groups are surrounded in some way by the 8 binding electrons arranged in one plane, there is likely to be a strain or partial distortion of the symmetry of the M_{32} and M_{33} electron orbits, with a corresponding decrease in the magneton numbers compared with those of the simple salts. Actually there is a small decrease in the magneton numbers in both the nickel and the copper compounds, 13 in place of 16 and 9 in place of about 10 respectively. The strain postulated may be similar to that supposed to exist in unsaturated organic compounds, since the fourfold coordination compounds may be looked upon as unsaturated, for of the 6 corners of the octahedron of the sixfold compounds, 4 lying in one plane are occupied, but the axial positions are vacant.

Many more experimental data will be required before the properties of the fourfold compounds can be explained with any certainty. Rosenbohm only gives measurements for five such compounds of definitely known structure, two for nickel and three for copper. A further investigation of the magnetic properties of the coordination compounds, preferably over as extended a range of temperature as possible, would be of great value.

A point of great importance must be mentioned here. It will be noticed that in the three schemes considered above a distinction has been made between simple and complex salts and that this distinction has been retained so far in the discussion. Such a distinction cannot, however, be maintained. Thus, for example, the typical "simple" salt, $NiCl_2 . 6H_2O$, is according to Werner to be regarded as a sixfold coordination compound, and the formula is to be written $[Ni(OH_2)_6] . Cl_2$. The other "simple" salts also require to be interpreted in the light of such views. It will then be seen that the distinction made by Cabrera between the simple and complex salts, that in the latter there is a preferential completion of the M_{33} sub-group in the sixfold compounds, cannot be maintained. The hypothesis must be revised or altogether rejected. It is hoped to discuss the question from the point of view that the "simple" salts are in reality also coordination compounds in a further paper. The standpoint may be taken that the distributions of electrons proposed by Cabrera for the "simple" and the complex salts, with the suggested modification in the case of the fourfold compounds, are probably correct but that the reasons put forward in support of them require revision.

The Davy-Faraday Laboratory,
The Royal Institution,
Albemarle Street, London, W. 1.
Feb. 4th, 1926.

VII. *X-Ray Term Values, Absorption Limits, and Critical Potentials.* By Edmund C. Stoner, *Ph.D.* (*Cambridge*), *Lecturer in Physics at the University of Leeds* *.

§ 1. Introduction.

DURING the last few years a large number of investigations have been made on the critical potentials for the excitation of soft X-rays in solid elements subjected to electronic bombardment. In the usual arrangement, electrons from a hot filament are accelerated towards a target under a variable applied voltage, and the photo-electric effect of the emitted radiation on a subsidiary electrode is measured. Precautions are taken to ensure the absence of effects due to electron scattering and secondary electron emission. The photo-electric current, expressed as a fraction of the primary current, is plotted against the accelerating voltage. The curves obtained usually show a number of more or less definite bends, and the corrected voltages at which these occur are taken to correspond to critical potentials for the excitation of X-rays. With a particular apparatus, the critical points are generally reproducible to one or two volts, and there can be little doubt as to their reality. The character of the bends, however, even for the same critical point, shows considerable variability, depending in some obscure manner on the precise conditions. Although different investigators' results may be in rough agreement as to some of the points, in general the agreement is far from complete, particularly as to the number of points observed.

Some of the critical points have been interpreted as corresponding to definite X-ray levels in the atoms, and it is the purpose of this paper to discuss how far this correlation is possible. As the number of critical points usually exceeds the number of energy levels, and as different investigations yield different values, the identification tends to become very arbitrary when applied to levels for which X-ray data are not available. In the interests of brevity, the discussion here will be mainly confined to the elements Cr (24) to Zn (30). The whole series have recently been investigated by Andrews, Davies and Horton [1], and particular members by Thomas[2] (Fe, Co, Ni, Cu) and by Richardson and Chalklin[3] (Fe, Ni).

---

* Communicated by Prof. Whiddington, F.R.S.

[1] Andrews, Davies and Horton, Proc. Roy. Soc. cx. p. 64 (1926).

The measurements of the wave-lengths of some of the L series lines of these elements by Thoræus[4] enable fairly complete energy level schemes to be drawn up. Some of the difficulties which emerge in making computations of this kind, based on the combination principle, are discussed (§ 2).

The problem of the fine structure of X-ray absorption edges is next considered, partly for its own interest and partly because some attempts have been made to correlate the multiplicity of critical points with this fine structure[1] (§ 3).

The experimental critical potential results are briefly summarized (§ 4). Various interpretations which have been given are then discussed and some further suggestions are put forward (§ 5). The paper closes with a summary (§ 6).

§ 2. COMPUTATION OF TERM VALUES FROM X-RAY DATA.

The term values for the energy levels expressed in Rydberg units which may be derived from the X-ray data are set out in Table I. for the elements Ti to Zn. The observed values for the K absorption limit are those of Lindh[5], Chamberlain[6], and Walter[7], which are believed to be the most accurate available. The values for the $K\gamma$ line are those of Siegbahn.

Under [K] are given the values for the K edge which have been taken as the basis of the subsequent calculations. In arriving at these values it has been assumed that they increase regularly in passing through the sequence of elements (actually $\sqrt{\frac{\nu}{R}}$ values were considered); consistent with this, values as close as possible to those observed have been taken. The procedure is slightly arbitrary, but seems justified by the fact that the [K] values do not differ from those observed by more than these differ from each other. (The precise significance of [K] will be considered in the next section.)

The values derived for the other levels depend essentially on those assumed for [K], and small relative errors in the determination of the K edge will result in large relative errors for the levels of smaller energy. It is probably for

[2] Thomas, Phys. Rev. xxv. p. 319, and xxvi. p. 739 (1925).
[3] Richardson and Chalklin, Proc. Roy. Soc. cx. p. 247 (1926).
[4] Thoræus, Phil. Mag. i. p. 312 (1926).
[5] Lindh, *Zeit. f. Phys.* xxxi. p. 210 (1925).
[6] Chamberlain, Phys. Rev. xxvi. p. 525 (1925).
[7] Walter, *Zeit. f. Phys.* xxx. p. 350 (1924).

TABLE I.—$\frac{\nu}{R}$ Term Values.

Element.	K observed.	Kγ.	[K].	L_{I}.	L_{II}.	L_{III}.	M_{I}.	$M_{II, III}$.	$M_{IV, V}$.
22 Ti ...	365·8 (L) 366·0 (C)	365·6	365·8	(41·0)	34·0	33·6		2·6	
23 V ...	402·7 (L) 402·9 (O)	402·4	402·7	(45·9)	38·5	38·0		3·0	
24 Cr...	441·0 (L) 441·3 (C)	440·9	441·3	(51·0)	43·2	42·5	(5·9)	[3·7]	·2
25 Mn .	481·6 (L)	481·3	481·7	(56·3)	(48·1)	47·2	(6·2)	3·6	·2
26 Fe...	523·5 (L)	523·5	523·8	(61·9)	53·2	52·2	6·9	4·0	·3
27 Co...		567·6	567·8	(67·7)	58·6	57·4	7·3	4·3	·3
28 Ni ...	613·8 (W)	613·5	613·8	(73·8)	64·3	63·0	7·9	5·1	·3
29 Cu...		661·3	661·7	(80·3)	70·4	68·9	8·9	5·8	·4
30 Zn...	711·4 (W)	711·3	711·5	(87·2)	(76·9)	75·2	9·9	6·6	·7

this reason that the $M_{II,III}$ values for these elements in the original Bohr and Coster tables show such marked irregularities.

Walter[8] has drawn up a fairly complete energy-level scheme for the elements Ti (22) to Te (52) from the wave-length data then available. Recognizing the lack of precision in some of the K edge wave-length measurements, he computed [K] by assuming that it exceeded Kγ by a fractional amount p:

$$\left(\frac{\nu}{R}\right)_K = \left(\frac{\nu}{R}\right)_{K\gamma}\left(\frac{100+p}{100}\right).$$

On the basis of measurements for Ni, Rh, and W, Walter assumed that p varied linearly with atomic number:

$$p = \cdot 010\,(Z-22).$$

The Kγ line corresponds to the transition $N_{I,I} \rightarrow K$, so that it is virtually assumed that the level (which may be the boundary of the atom) to which the electron is removed in the K-edge transition differs from $N_{II,III}$ by an amount which increases regularly from zero for Ti. This assumption seems difficult to justify for elements such as those here in question, in which $N_{II,III}$ is a virtual level, though a linear relation of the kind employed may hold roughly for elements of higher atomic number than those in which the $N_{II,III}$ levels are first fully occupied. It is true that the [K] values obtained in this way will differ relatively little from those in the [K] column of Table I. (as may be seen from the values there given for the Kγ lines); but the procedure is somewhat unsatisfactory, and it seems better to take [K] values based on those actually observed for elements for which precise measurements have been made—particularly as the Kγ line, as has been pointed out by Coster[9], is very weak and difficult to measure accurately for elements of low atomic number.

In the computation of the other levels, the following combination equations have been used:—

$$\begin{aligned}
L_{III} &= K - K\alpha_1,\\
L_{II} &= K - K\alpha_2,\\
M_{II,III} &= K - K\beta,\\
M_{I} &= L_{II} - Ll = L_{III} - L\eta,\\
M_{III\,V} &= L_{III} - L\alpha = L_{II} - L\beta_1.
\end{aligned}$$

---

[8] Walter, *Zeit. f. Phys.* xxx. p. 357 (1924).
[9] Coster, *Zeit. f. Phys.* xxxi. p. 898 (1925).

The $\frac{\nu}{R}$ values of the K lines have been taken from the tables in Sommerfeld's *Atombau* (4th ed. 1925, p. 260).—For these elements the measurements are mainly those of Siegbahn. The L-line values are taken from Thoræus[4], who has measured $L\alpha$ and $L\beta$ for Cr to Zn, and $L\eta$ and Ll for Fe to Zn. The bracketed values for M_I for Cr and Mn are extrapolated. For the calculation of L_I, the $L\beta_3$ and $L\beta_4$ lines are required ($L\beta_3 = L_I - M_{III}$, $L\beta_4 = L\ - M_{II}$), and these have not yet been measured. In order to obtain an estimate of L_I, it has been assumed that L_I and L_{II} form a normal screening doublet, the separation being given by

$$\sqrt{L_I} - \sqrt{L_{II}} = 0{\cdot}57$$

(*cf.* Sommerfeld, p. 458).

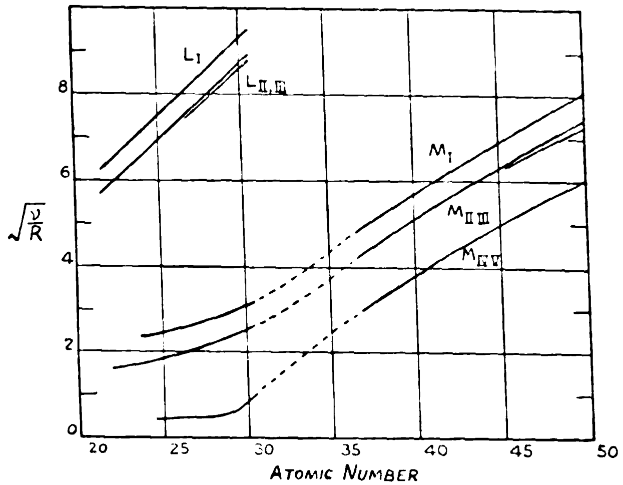
The numbers so obtained show a fairly regular progression with atomic number, except in the case of $M_{II,III}$ for Cr. Slight irregularities may be real—though little can be said with certainty on this point at present,—but the divergence in this case is so large that it is probably to be attributed to some error in the measurements. There can be little doubt as to the substantial accuracy of the general order of magnitude of the term values deduced and as to their sequence. The M_I and $M_{II,III}$ values are coherent with those of elements of higher atomic number, as is shown by plotting $\sqrt{\frac{\nu}{R}}$ (see fig. 1). (Walter's values are taken for elements of higher atomic number.) There is no indication of unexpected peculiarities in the curves in this region such as are suggested by some of the values which have been attributed to the levels on the basis of critical potential measurements. (See, for example, the curves given by Sommerfeld, p. 572.)

The most definite value for the $M_{II,III}$ level in this region is probably that deduced by Millikan and Bowen[10] from lines in the ultra-violet spectrum of Ca (20). They give for M_{II}, $\frac{\nu}{R} = 1{\cdot}8387$, $\sqrt{\frac{\nu}{R}} = 1{\cdot}3560$; for M_{III}, $\frac{\nu}{R} = 1{\cdot}8104$, $\sqrt{\frac{\nu}{R}} = 1{\cdot}3455$. These values fall in line with those of Table I.

---

[10] Millikan and Bowen, Phys. Rev. xxiii. p. 1 (1924).

Fig. 1.—$\sqrt{\frac{\nu}{R}}$ Values for Terms.



In Table II. the term values required in the critical potential discussion are given in volts $\left(V=13{\cdot}54\frac{\nu}{R}\right)$. An interpolated value has been used for Cr $M_{II,\,III}$ corresponding to 3·4 in Table I. in place of 3·7.

TABLE II.—Term Values. Volts.

Element.	L_I.	L_{II}.	L_{III}.	M_I.	$M_{II,\,III}$.
24 Cr ...				(80)	(46)
25 Mn...				(84)	49
26 Fe ...	(838)	720	706	93	54
27 Co ...	(917)	793	777	99	58
28 Ni ...	(999)	871	835	107	69
29 Cu ...	(1124)	953	933	120	78
30 Zn ...				134	89

§ 3. THE FINE STRUCTURE OF X-RAY ABSORPTION EDGES.

It was at first believed that X-ray absorption edges were simple in structure, there being a sudden increase in absorption, followed by a gradual falling off, as the frequency of the incident radiation increased, passing through the critical frequency corresponding to the energy required to remove an electron from a level completely out of the atom (that is, to give it a total energy greater than zero). Photographic investigations of Fricke, Lindh, and others showed that in many cases the long wave-length edge was marked by an absorption line followed by one or more regions of weaker and stronger absorption before the uniform continuous absorption region was reached. Kossel had predicted that a fine structure should be found, corresponding to the removal of the electron to various possible virtual (optical) orbits at frequencies lower than that at which continuous absorption began. This interpretation has been generally accepted, but it does not seem to have been brought into any close relation with the fine structures actually observed, and it seems desirable to consider the observations and theory somewhat more closely, particularly in regard to the order of magnitude of the separations of the "remarkable points" of the fine structure.

When pure elements are examined, at least when these are metallic, in general no fine structure is observed. This statement is supported by the work of Fricke[11] (Mg, Al), Lindh[5] (Ti, V, Cr, Mn, Fe), and Chamberlain[6] (Ti, V, Cr).

For elements such as P, S[11], and Cl[12], however, whose molecules are polyatomic, fine structure is found. The fact that a fine structure is not observed for metallic elements—whose molecules in general may be regarded as monatomic, and as not being markedly distorted from their "free state" form as regards level energies—does not necessarily mean that it is non-existent, but that it is confined within a range of wave-lengths which is so small that it is unresolved, owing to slit widths, slight non-homogeneity of the radiation components, and scattering. On Fricke's photographs the distance of the point at which increased absorption begins to the point at which it is a maximum corresponds to 2·7 and 4·9 volts for Mg and Al respectively. Richtmyer[13] has recently considered in great detail the correction necessary for finite slit width; he concludes from his measurements (by the ionization method) of absorption near the AgK limit that the jump occurs within ·0002 A.U. This, though small (about ·04 per cent. λ_K), corresponds to a voltage range of about 10, which is of the order of magnitude of the optical energy level differences.

---

[11] Fricke, Phys. Rev. xvi. p. 202 (1920).

[12] The case of S and Cl is discussed in detail by Siegbahn: Spectroscopy of X-Rays, Eng. transl. p. 143 (Oxford, 1924).

[13] Richtmyer, Phys. Rev. xxvi. p. 724 (1925).

With compounds, the continuous absorption edge is shifted to a shorter wave-length, but on the long wave-length side of this a white absorption line is generally found (Coster[14], Lindh[5], Chamberlain[6]). Within the limits of experimental error the long wave-length edge of the absorption line coincides with the wave-length of the absorption edge of the free element. It has been supposed that the white line is actually due to the free element which may be present owing to oxidation or reduction processes brought about by the X-rays themselves, and Chamberlain brings forward some evidence in support of this view. The persistence of the white line and its intensity, however, in many cases where the amount of free element present must be very small, suggests that it may be an essential characteristic of the absorption of the compound, though its intensity may be increased if some of the free element is present as well. Thus Nishina[15] finds an intense white line characterizing the L_{III} absorption edge of compounds of the trivalent elements in the group Pr (59) to Ho (67); there is a second white line on the short wave-length side; and sometimes a third more diffuse line of still shorter wave-length is measurable.

The order of magnitude of the separation between the long wave-length edge of the white absorption line (K_1), corresponding to the edge for the free element, and the continuous absorption edge (K_2) on the short wave-length side may be illustrated by some values (in volts) given by Lindh.

Table III. shows clearly the dependence of the separation K_2-K_1 (or the shift of K_2) on the valency of the element concerned. The higher the valency the greater the separation. This correlation has been recognized for some time (Lindh, Siegbahn), but its significance in providing a possible clue to the fine structure problem does not seem to have been fully realized.

There can be little doubt as to the theoretical soundness of

---

[14] Coster, *Zeit. f. Phys.* xxv. p. 83 (1924).

[15] Nishina, Phil. Mag. xiix. p. 521 (1925).

Kessel's view, and this must form the basis of any explanation. For the normal atom the lowest frequency radiation which can remove an electron from a K level will be that with the quantum energy corresponding to the transition from the K level to the lowermost unoccupied virtual orbit to which a transition can occur—that is, in general, to the *np* optical orbit with the smallest *n*. Such an orbit may conveniently be referred to as "peripheral," and the energy of an electron in it will not differ widely from that of the most loosely bound electrons in the atom.

TABLE III.

$K_2 - K_1$. Volts. (Lindh.)

TiO_2.........	17·0	$MnSO_4$......	9·7
V_2O_5	14·0	MnO_2	15·2
$Cr_2(SO_4)_3$...	11·9	$KMnO_4$ ...	20·0
$K_2Cr_2O_7$ ...	19·7	$FeSO_4$......	9·0
		$Fe_2(SO_4)_3$..	13·9

Transitions should then be possible to *np* orbits of higher *n*; there should be a series of absorption lines crowding together to a head where continuous absorption begins, corresponding to the removal of the K electron to the "boundary" of the atom. By analogy with optical spectra, however, it may be supposed that the probability of absorption of the first line is much greater than that of higher members. The structure anticipated for a K edge would then be, proceeding from longer to shorter wave-lengths, an absorption line followed by a region of smaller absorption which increases to the head where continuous absorption begins and then falls off gradually. The line absorption, however, has not been definitely observed for pure elements. If the above view is correct, this is due to the fine structure region being so small that resolution is not obtained. The "fine structure range," as it may be called, will depend on the energy of the lowermost *np* term to which a transition is possible. The order of magnitude of this may be readily calculated from the optical data. Thus for Mg the singlet and triplet $3p$ terms have energies corresponding to 3·3 and 4·9 volts. A fine structure within this range would hardly be observed. For ionized atoms, however, the fine structure range would be much increased. This may be illustrated by considering the energies of the lowermost optical p terms in a series of atoms:—

Approximate Energies of Lowermost Optical p terms.

($n=3$.) Volts.

Na	Mg^+	Al^{++}	Si^{+++}
3	11	21	34

Ionization would result in an increase in the fine structure range, with an increased possibility of resolution.

The above numbers can only be regarded as giving a rough idea of the order of magnitude to be expected, for although the field round an ion in a solid compound (*e.g.* round Mn^{++++} in MnO_2) will approximate to that round a free ion, it will be modified by the influence of the neighbouring ions of opposite charge.

That the "white line" should occupy approximately the same position for compounds in which the element has different valencies, and that this coincides with the edge for the free element, is readily intelligible.—The work required to remove a K electron to the boundary of an atom may be regarded as made up of that required to remove it to the peripheral orbit together with that to remove it from the "periphery" to the "boundary"; the first part will be little changed, as outer electrons, normally moving in peripheral orbits, are removed in different stages of ionization (or with increasing valency), but the second part will increase (with increase in the field beyond the periphery). In particular, the first part will be more nearly constant the larger the number of electrons moving in peripheral orbits of approximately equal energy.

The view that the K edge, as ordinarily measured, does not correspond to complete ionization is supported by the fact that when the energy of the $M_{IV,V}$ level for the first series of transition elements is calculated from the X-ray data (see Table I.). it comes out to be considerably smaller than would be anticipated from the optical spectra data. Thus the energies of the levels calculated will all be smaller than those corresponding to complete removal of an electron from them to the boundary by a quantity of the order of a few volts. The exact quantity could only be calculated if the precise nk level to which the K electron is removed were known, and if the energy of this could be calculated from the optical spectra.

The question arises as to what is the lowest peripheral level to which a K electron may be removed in the neutral atom. Normally it would be expected that it would be a level for which $k=2$: for the elements here considered, the $N_{II,III}$ level. The absorption line would not then necessarily be of the same wave-length as $K\gamma$, for the $K\gamma$ line is usually supposed to be due to a transition in an atom which has completely lost a K electron, so that $K\gamma$ would be of slightly longer wave-length than the absorption line. The problem, however, is complicated by the fact that the usual classification of X-ray levels (*e. g.* with five M levels, with $k=1$ for M_I, $k=2$ for $M_{II,III}$, $k=3$ for $M_{IV,V}$) only holds when these levels have their full complement of electrons. For the transition elements the $M_{IV,V}$ levels are being built up, and the N levels contain only a few electrons (usually one or two). The appropriate k values are in the nature of resultants (denoted by l in the recent work of Heisenberg and Hund), so that a number of electrons each characterized by $k=3$ may give rise to a configuration corresponding not only to D terms, but also to S, P, F, etc. This has a close connexion with the fact that changes of configuration involving double electron jumps may occur. The determination of the precise nature of the lowermost level to which a K electron can be transferred by the absorption of radiation must therefore await further developments in the analysis and interpretation of the optical spectra of the elements concerned.

As already mentioned, Nishina's observations on the structure of the L_{III} edge for Ho[15] ($Ho_2(SO_4)_3$ + aq. was used as the absorbing substance), three components were found; the separations being 34 and 89 volts. This would seem to require a more complicated explanation than that given above for the K edges of the elements of lower atomic number, and is left as an unsolved problem. The structure is possibly to be correlated with the fact that in the rare earth elements there are a number of levels (in the N, O, P groups) in an incomplete state, so that there are a greater number of possibilities of transition to levels which, in the ionized atom, may differ considerably in energy.

§ 4. CRITICAL POTENTIALS. EXPERIMENTAL RESULTS.

The critical potentials found in recent investigations by a number of workers for the elements here considered are set out in the following tables.

TABLE IV A.

Critical Potentials for Cr to Zn.

Andrews, Davies, and Horton [1] (below 230 volts).

	g.	*f.*	*e.*	*d.*	*c.*	*b.*	*a.*
24 Cr		60	70		143	160	173
25 Mn		68	83	100	152	174	184
26 Fe	47	73	99	106	166	181	
27 Co			94	113	171	191	
28 Ni			104		178	196	
29 Cu			112		193	206	
30 Zn			119		200	214	

TABLE IV B.

Critical Potentials for Fe to Cu.

Thomas [2] (above 350 volts).
Rollefson [16] (600–700 volts).

Fe (T.)		639	704	818	
,, (R.)	618	637	697		
Co (T.)		705	764	873	950
Ni (T.)		774	833	948	1017
Cu (T.)		820	929	1017	

TABLE IV C.

Critical Potentials for Iron.

Tables IV C and IV D :—
Richardson and Chalklin [3] (40–600 volts).
Rollefson [16] (30–185 volts).
Chu [17] (0–120 volts).

R. and C.......	46	51	64	76		85	95	108	115		138
Rollefson	47				82		95			130	
Chu		52	68		80						
R. and C.......						190	221	241	270	288	498
Rollefson	141	147	153	160							

TABLE IV D.

Critical Potentials for Nickel.

R. and C.......	39?			80?	89	99	140	245	316	335?
								393?	433?	532?
Chu		49	75			98				

---

[16] Rollefson, Phys. Rev. xxiii. p. 35 (1924).
[17] Chu, Journ. Franklin Inst. 200. p. 629 (1925).

The above tables summarize only a few of the investigations which have been made, but they will be sufficient to serve as a basis for the consideration of the general character and coherence of the results. (For a comprehensive survey of the values obtained by different workers for Fe and Ni, Richardson and Chalklin's paper may be consulted, and that of Andrews, Davies, and Horton for the elements of Table IV A, below 230 volts.)

It should first be noted that the number of critical points found varies very greatly. Thomas, working with large thermionic currents (·5 to 4 milliampere), taking great precautions to ensure steadiness, and varying the voltage by small intervals, obtained over forty breaks in the curves for Fe, Co, and Ni below 350 volts, and over twenty for Cu below 90 volts. These breaks were interpreted as ionization or resonance breaks according as the portion of the curve above showed an upward or downward concavity. In view of Richardson's observations that the character of a break may vary considerably in different experiments, it seems doubtful whether the classification has any significance, though Thomas found that the curves were closely reproducible. In distinction to Thomas, Chu, working with small thermionic currents (of the order of 10 microamperes), found well-defined breaks, few in number, as indicated in the above tables. (Only three were found for Fe and Ni, and five for Cu—at 30, 49, 62, 79, and 90 volts.)

Owing to the large number of breaks found by Thomas, some of his values may usually be found fairly close to those of other observers; but when experiments in which the number of critical points is more limited are compared with each other, there is so little general agreement that it almost seems as if agreement is fortuitous even when it does occur. This is seen at once by inspection of Tables IV A, C, and D. For iron there is some agreement as to a critical point in the neighbourhood of 50 volts, but otherwise it is only by considerable forcing that the results can be regarded as mutually supporting. This cannot be attributed to errors in correcting the measured voltage for initial velocity, and for the work function, for there is disagreement as to the sequence of values as well as their absolute magnitude. It is clear that the critical potentials, at least in the low voltage region, do not yield direct and simple information as to the soft X-ray energy levels in atoms. They must, however, have some connexion with them, and some of the suggestions which have been made will now be considered.

§ 5. CRITICAL POTENTIALS. SUGGESTED INTERPRETATIONS.

As Andrews, Davies, and Horton have examined the longest sequence of elements, their interpretations of their results will be considered first. They suggest that the points *g, f*, and *e* (Table IV A) are associated with transitions from the $M_{II,III}$, and the points *d, c, b, a* from the M_I level; *g* and *d* corresponding to transitions to the periphery, and the other points to virtual orbits beyond the periphery. The consideration of the magnitudes of the differences of energy associated with such transitions in § 3, however, casts doubt on this interpretation. The range of voltage for one set of transitions should not be greater than the fine structure range (depending on the energy of the lowermost unoccupied optical level), and this for the *neutral* atom is of the order of a few volts. On the interpretation given, moreover, the work required to remove an $M_{II,III}$ electron to the boundary would correspond in the case of iron, for example, to the limit of the series 47, 73, 90—it would be greater than 90 volts: similarly, the $M_I \rightarrow$ boundary transition would correspond to an energy greater than 180 volts. (The limit of the series 106, 166, 181.) Both of these values are far in excess of those calculated from the X-ray data (Table II.). There are thus two reasons indicating that the view requires considerable modification.

Other workers have also attempted to account for the critical points in a general way as associated with ionization and resonance transitions. Richardson and Chalklin have made the additional suggestion that transitions may be possible to orbits within the atom which are normally unoccupied. It must be remembered, however, that the last bound electrons enter orbits in which they are most firmly bound, so that the postulate of unoccupied orbits having greater (negative) energy—which is necessary if the hypothesis is to explain a wider range of facts than the usual one—raises many difficulties. A further suggestion of Richardson and Chalklin's—that there may be discontinuities in the general radiation—is so far without independent experimental support.

Multiple impact, as has been mentioned by Thomas and others, will account for critical potentials which are the sum of those corresponding to single impact critical potentials—an electron having sufficient energy, after a "resonance" encounter, to produce ionization or resonance in another atom.

The suggestions so far considered would lead to the anticipation of critical potentials crowded together near X-ray energy level values (corresponding to the narrow virtual orbit and fine structure range), and of potentials which are the sum of these. They do not, however, seem capable of explaining many of the relatively widely spaced points which are observed.

A comparison of Tables IV. and II. shows that critical potentials are sometimes observed which can be fairly definitely associated with X-ray levels. In Thomas's results it is particularly striking that although he found a large number of breaks at lower potentials, above 350 volts he found only those recorded in Table IV B. (It should be noted, however, that Richardson found a few breaks in the intermediate region for Fe and Ni, though he regards those for Ni as doubtful.) Of these the series, for Fe, Co, Ni, and Cu, of 704, 764, 833, and 929 agree reasonably well with the values 706, 777, 853, and 933 computed for L_{III} from the X-ray data. The next group of values are considerably above those computed for L_{II}, and rather smaller than those for L_I; while the largest critical potentials observed (950 for Co, and 1017 for Ni) are larger than the L_I values (approximately 917 and 999). As to the M levels, Horton's *g* value for iron of 47, with those of other observers (Table IV C) of 46, 47, 51, and 52, agree fairly well with the computed value of 54 for the $M_{II,III}$ level; but in the absence or disagreement of the corresponding point for Ni this is not very satisfying. Horton's *e* values are fairly close to those computed for M_I, but are consistently lower by an average value of about 5 volts.

Critical potentials are undoubtedly to be associated with transitions of electrons from particular levels; and some of the higher values found (such as Horton's *a*, *b*, *c* groups) must be due to multiple impact. The problem which remains is to account for some of the higher values found where multiple impact seems inadequate to explain the values even qualitatively, and to account for values much lower (such as some of those of Thomas in the L region) than the computed term values.

The suggestion is made that an explanation of many of the apparently anomalous results is to be sought in the consideration of the excitation potentials of atoms which have already lost one or more electrons, either from loosely bound groups, or from groups more "deeply seated" in the atom. Under the experimental conditions there must generally be present atoms which have lost a number of outer electrons. As discussed in § 3, the amount of work then required to remove an electron from, say, the K level completely to the boundary of the atom will increase in passing from the neutral to the singly, doubly, ... charged atom by an amount approximately equal to that required to remove the series electron from the atom in its different stages of ionization; these differences being of the same order of magnitude as those observed in the experiments. A simple correlation of the results is, however, hardly feasible owing to the many different possibilities, the inadequacy of the optical spectra data, and the indefinite experimental conditions. If electrons have been removed from say an M level, then the possibility arises of there being a critical potential corresponding to the removal of an L electron to the vacant space created. This potential will be lower than the L critical potential by an amount approximately equal to that of the M level concerned. Some of Thomas's L values are in rough agreement with this view. The critical potentials will not necessarily agree with X-ray line values owing to the complicated reorganization processes which may occur.

The ionization of a particular atom may be brought about not only by direct impact, but by absorption of radiation from other atoms. This makes an additional complication, for it means that it will be almost impossible from critical potential experiments alone, even if multiple impact effects could be excluded, to obtain any precise idea of the energy levels, unless there is some information available as to their order of magnitude from spectroscopic data—particularly in the case of the levels of smaller energy. It would seem that experiments in which the primary current density is as small as possible would lead to fewer breaks being observed, which might be more easily interpreted; but the technical difficulties would then become greater. The whole question of the relative probability of single and multiple impact and multiple excitation effects is involved.

The recent development of the technique for the investigation of long X-rays and short ultra-violet rays means that data will soon be available from which more complete and accurate energy level schemes may be drawn up. Apart from this, the most direct way of investigating the energy level values is probably that of measuring the lines in the magnetic spectrum of the electrons emitted photo-electrically under the influence of monochromatic incident radiation as used so successfully by Robinson, Whiddington, de Broglie, and others. (If the precision and resolving power could be sufficiently increased, such investigations should also be able to shed further light on the fine structure problem, for it is the energy required to remove an electron completely from the atom which can be determined.) Critical potential investigations, carried out under well defined conditions, will then become of great interest and value in connexion with many problems, though they do not seem adapted for the direct precise determination of energy level values.

§ 6. SUMMARY.

The paper deals with term values, absorption limits, and critical potentials, with particular reference to the elements titanium (22) to zinc (30).

The term values are computed from the X-ray data, and are shown to fit in coherently with those of elements of higher and lower atomic number. The limitations of the method are considered.

The fine structure of absorption edges is discussed, and it is concluded that the term values correspond to the energy required to remove an electron to the lowermost possible unoccupied optical level in the atom. For a neutral atom this will differ by only a few volts from that corresponding to removal to the boundary, but the difference increases with successive stages of ionization of the atom. This is correlated with the range of fine structure observed for compounds. The general character of the edges, and the order of magnitude of the separations between the fine structure components are accounted for.

The critical potential results of a number of investigators are compared, and some of their interpretations criticised. In addition to the usual explanations, it is suggested that some of the points correspond to critical potentials for atoms which have been ionized by the loss of outer or inner electrons. These potentials may be higher or lower than those for the neutral atoms. It is shown that critical potential experiments are unsuitable for the direct precise determination of atomic level energy values, particularly when these are small.

Department of Physics,
University of Leeds.
March, 1926.

Note added to proof.—Using high resolving power, Coster and van der Tuuk ('Nature,' cxvii. p. 586, April 24, 1926) have recently found fine structure in the K absorption edge of argon. They consider that this is probably to be explained as due to transitions to different *p* levels, the separation of the two edges observed (about 1·7 volts) being of the right order of magnitude. The interpretation is in agreement with that of § 3.

VIII. *The Crystalline Structure of Anhydrite.* *By* E. C. S. Dickson, *B.A., Ph.D., Senior Lecturer in Physics, Manchester University, and* W. Binks, *B.Sc. Manchester* *.

1. ANHYDRITE, the stable form of anhydrous calcium sulphate $CaSO_4$, crystallizes in the bipyramidal class of the rhombic system. Its axial ratios are given by von Groth as

$$a : b : c = 0{\cdot}8932 : 1 : 1{\cdot}0008.$$

Natural crystals generally show only the three pinacoid faces: cleavage parallel to the (010) and (001) faces being perfect, and parallel to the (100) face less perfect. The specific gravity is 2·96.

The pseudo-tetragonal axial ratio $b : c$ distinguishes anhydrite from the chemically analogous substances barytes, celestine, and anglesite, the structures of which have been determined by James and Wood †. Its structure might therefore be expected to be relatively simple, and to throw further light on the dimensions of the SO_4 group, which has been shown by Bradley ‡ to approximate to a tetrahedron, the centres of the oxygen atoms lying at the corners and the sulphur atom at the centre, the distance S to O being about 1·5 to 1·6 Å.

2. *Experimental Results.*

Natural crystals from various sources were examined by the usual ionization spectrometer method. Cleavage faces were lightly ground before use, the other faces being ground on the crystals with carborundum. It was found convenient to embed the crystal entirely in a mass of dental wax before grinding, to prevent shattering of the face.

All intensities were compared ultimately with that of a standard (400) rock-salt reflexion (actual second order reflexion), but substandards were employed for some of the weaker spectra. Owing to the small size of some of the faces available the accuracy of the intensity measurements, especially at low angles of incidence, is questionable. K_α radiation from a molybdenum Coolidge bulb was employed throughout.

---

* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

† Proc. Roy. Soc. cix. p. 598 (1925).

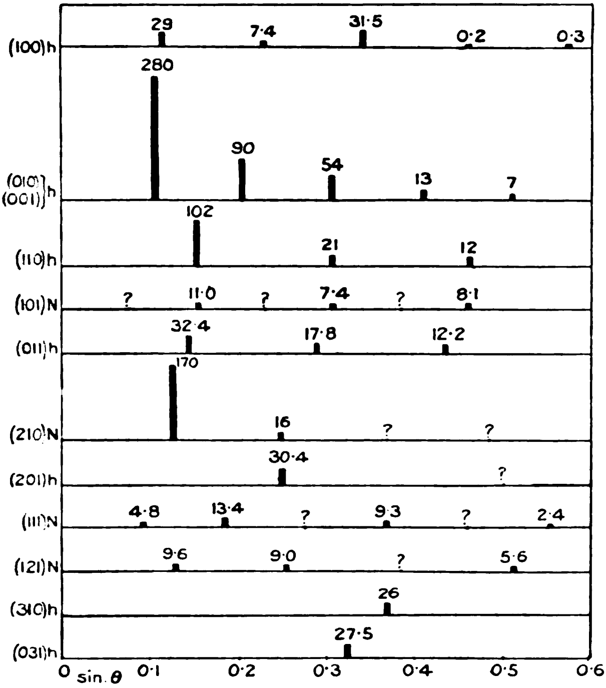
‡ Phil. Mag. xlix. p. 1225 (1925).

The following is a list of the faces examined:—

(100)	(110)	(210)	(031),
(010)	(101)	(201)	(111),
(001)	(011)	(301)	(121).

Fig. 1 shows graphically the distribution and intensity of the observed reflexions.

Fig. 1.



3. *Unit Cell and Space-Group.*

During the course of the present work a determination of the unit cell and space-group of anhydrite was published by Rinne, Hentschel, and Schiebold *. Their values for the dimensions of the unit cell are

$$a = 6{\cdot}21\ \text{Å}. \quad b = 6{\cdot}95\ \text{Å}. \quad c = 6{\cdot}96\ \text{Å}.$$

The corresponding values from measurements made by us during a preliminary survey of the crystal are:

$$a = 6{\cdot}19\ \text{Å}. \quad b = 6{\cdot}94\ \text{Å}. \quad c = 6{\cdot}94\ \text{Å}.$$

---

* *Zeitschr. f. Krist.* lxi. p. 164 (1925).

We do not regard our figures however as very reliable, and in our determination of the crystal structure we have used the former values.

The specific gravity shows that the cell contains four molecules.

Using the rotating crystal method, Rinne, Hentschel, and Schiebold identified the space-group of anhydrite as V_h^{17} in Schönflies's notation. The spectrometer measurements made by us are not sufficient for a unique determination of the group but they agree, as far as they go, with the exception of the (101) face. We were unable to detect the odd spectra from this face with our apparatus, so that only even spectra appeared to be present. Rinne, Hentschel, and Schiebold record the presence of a (303) reflexion, but qualify it as not quite certain.

Further corroboration of the space-group was obtained by means of a Debye powder-photograph, kindly taken for us by Dr. A. J. Bradley. It happens by chance that although the pseudo-tetragonal ratio of the b and c axes causes reflexions from certain faces to coincide on the powder-photograph, yet the presence or absence of certain lines provides useful criteria which confirm the space-group as V_h^{17}.

It must be remembered that, in the case of a Laue photograph of a single crystal, the pseudo-tetragonal ratio of the axes will be masked entirely by the true rhombic nature of the crystal, as can be seen by inspection of such photographs of anhydrite already published by Haga and Jaeger [*], and by Rinne [†]. The Laue diagrams show only two planes of symmetry at right angles.

Astbury and Yardley [‡] give the following criteria for the abnormal spacing of planes in the group V_h^{17} (their Q_h^{17}), when their axes are suitably transformed to fit the crystallographic axes of anhydrite.

All spacings of the general type $(h\ k\ l)$ are halved if $h+l$ is odd.

All $(o\ k\ l)$ spacings are halved.

4. *Symmetry Elements of the Group* V_h^{17}.

The symmetry elements of the group are given in full in Rinne, Hentschel, and Schiebold's paper [§] and in the tables of Niggli or Astbury and Yardley.

---

[*] *Akad. v. Wetensch. Amst.* xxiv. p. 460 (1915).

[†] II. *Mitteil. Ber. d. Sachs. Akad. d. Wissensch.* lxviii. p. 11 (1915).

[‡] Phil. Trans. Roy. Soc. A, ccxxiv. p. 225 (1924).

[§] *Loc. cit.* The reflexion planes given as $(010)_0$ $(010)_{\frac{1}{2}}$ should read $(001)_0$ $(001)_{\frac{1}{2}}$, and the symmetry centres printed as $[[\frac{1}{4}\ \frac{1}{2}\ \frac{3}{4}]]$, $[[\frac{3}{4}\ \frac{1}{2}\ \bar{\frac{3}{4}}]]$, should not have the minus signs.

The most important feature is the presence of two sets of intersecting reflexion planes, $(001)_0$ $(001)_{\frac{1}{2}}$ and $(010)_{\frac{1}{4}}$ $(010)_{\frac{3}{4}}$. Three sets of glide planes also occur: $(100)_0$ $(100)_{\frac{1}{2}}$; $(100)_{\frac{1}{4}}$ $(100)_{\frac{3}{4}}$; $(001)_{\frac{1}{4}}$ $(001)_{\frac{3}{4}}$ with glides of $b/2$; $(b+c)/2$; $a/2$ respectively. The positions of most of the symmetry centres, which are of three types, and of the digonal rotation and screw axes are shown in figs. 2 and 3, in Astbury and Yardley's notation.

5. *Possible Crystal Structures.*

The only attempt yet made to assign a structure to anhydrite, so far as we know, is an admittedly conjectural one used in a diagram by Rinne [*] merely to illustrate the transformation into the unstable β-modification. In this diagram the SO_4 group appears to be represented as having all its atoms in one plane parallel to one of the pinacoids, while the calciums and SO_4 groups are arranged on two interpenetrating face-centred lattices.

Such a structure would require the spectra from one pinacoid face to be normal in intensity, since all the atoms are concentrated in the planes, while the normal character of the reflexions from the two other pinacoids would be relatively weakened by oxygen atoms lying off the planes. Reference to fig. 1 shows that the outstanding feature of the observed intensities is the presence of identical reflexions from two of the pinacoids, approximating to normal type, while the third pinacoid yields spectra so far from normal that the sixth order (third actual spectrum) is larger than the second (first actual spectrum).

This arrangement would therefore not correspond to the facts.

If now we start with the assumption of a tetrahedral SO_4 group, as already found in the structure of lithium-potassium sulphate and in barytes, celestine, and anglesite, we can make certain deductions as to permissible positions of atoms in the unit cell from symmetry considerations alone.

The peculiar symmetry of a tetrahedron precludes placing the sulphur atom which occupies its centre at a centre of symmetry of the space-group. The only other possible arrangement of four atoms in the unit cell of this space-group, is to place them so that each atom lies on both sets of reflexion planes, *i.e.* on their line of intersection, with one degree of freedom only.

---

[*] *N. Jahrb. f. Min.* ii. p. 98 (1916).

As regards the position of the sixteen oxygen atoms, we might try to place them at the sixteen centres of symmetry. These centres, however, are situated on parallel planes $(010)_0$ and $(010)_{\frac{1}{2}}$, while the intersections of the reflexion planes, on which the S atoms are located, lie a quarter and three quarters along the *b* axis of the cell. On plotting the position of the centres, it is seen that no arrangement of four independent tetrahedra is possible, and this arrangement is also incompatible with the observed intensities from the (010) face.

It might still be possible for either eight or four oxygen atoms to be disposed in four separate manners at the three types of symmetry centre available (one eight-fold, two four-fold).

Now the eight-fold symmetry centres common to the unit lie at the corners of two contiguous parallelepipeds, and could only be regarded as forming pairs of interpenetrating tetrahedra, which would require the two sulphur atoms in each pair to occupy the same portion of space. These eight oxygen atoms would also be out of phase with the sulphurs for the (020) and (002) reflexions.

The positions of both sets of four-fold centres are such that they could not be grouped in tetrahedra round the S atoms. They would also be in phase with the S atoms for the (002) and out of phase for the (020) reflexions, rendering these spectra unlike. It appears then that none of the oxygen atoms can be at a symmetry centre.

An oxygen atom placed in a general position in the cell with coordinates $[[m, n, p]]$ introduces sixteen by the operations of symmetry. But if the position of these points is plotted, it is found that they cannot be arranged in tetrahedra with centres on the intersection of the reflexion planes.

The oxygens must therefore have either one or two degrees of freedom only.

Points with one degree of freedom may occupy two sets of positions. A four-fold one with coordinates $[[n, \frac{1}{4}, 0]]$; or an eight-fold one on the rotation axes parallel to the [001] axis. The four-fold set is represented by positions on the intersections of the reflexion planes, on which the S atoms are already placed. This is the only four-fold set of points in the cell except symmetry centres. All the oxygens would therefore have to lie on these intersections, which is impossible with tetrahedral groups.

The eight-fold set lies on the rotation axes parallel to the [001] axis, in groups of four points about the intersections of the reflexion planes. Oxygens in these positions could only form interpenetrating tetrahedra and would also be out of phase with the sulphur for the (020) and (002) reflexions.

Points with two degrees of freedom are confined to the reflexion planes, and each independent point forms a set of eight in the cell. If now we place a regular tetrahedron with two of its oxygens in one reflexion plane, equidistant from the other, and the two other oxygens similarly in the intersecting reflexion plane, the conditions of symmetry are fulfilled and the sixteen oxygens may be regarded as made by the operations of symmetry on two atoms, involving only two independent parameters.

This at once introduces an enormous simplification in the determination of the crystal structure. The SO_4 group as a whole has only one degree of freedom, namely movement along the axis of intersection of the reflexion planes. Its position is therefore dependent on a single parameter. The uncertainty of size of the SO_4 group introduces a second parameter, so far as intensity measurements are concerned, which may be regarded as the distance between oxygen centres in the tetrahedron.

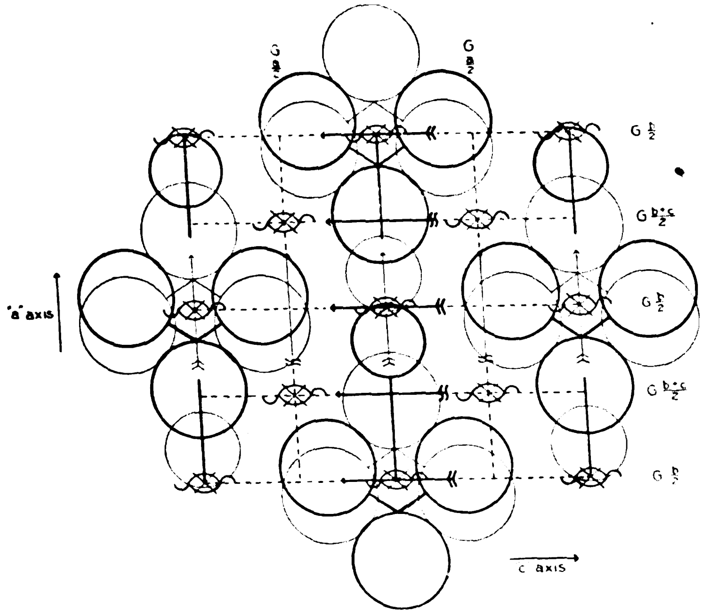
The four calcium atoms still require to have places assigned to them in the unit cell. Two possible arrangements would be to situate them all at either of the two sets of four-fold symmetry centres. Intensity considerations show that they would then be in phase with the sulphurs in the (002) and out of phase in the (020) reflexion, so that these spectra would be of unequal intensities.

The only other possible distribution of four atoms in the cell is to place them similarly to the sulphurs on the axis of intersection of the reflexion planes. Their position will therefore also be determined by a single parameter, the possible variation of which is limited by the freedom of movement of the calcium atom between consecutive SO_4 groups. If we take the known distance between calcium and oxygen centres in other crystals and assume it to have approximately the same value in anhydrite, it is clear that any displacement of the calcium from a position midway between the SO_4 groups must be small unless serious distortion of the SO_4 tetrahedron be postulated.

Once we assume the dimensions of the SO_4 group to be fixed, and the calciums limited to positions nearly midway between two SO_4 groups, the problem of determining the approximate structure reduces to that of finding a single parameter. This may be thought of as defining the displacement of two contiguous (010) sheets of atoms which slide in opposite directions along the [100] axis.

When the operations of the various glide planes are considered, we see that each sheet consists of similarly oriented tetrahedral SO_4 groups arranged on a face-centred pattern, the calcium atoms lying in a similar pattern between consecutive SO_4 groups on the same axes. This is shown by fig. 2. The orientation of SO_4 groups is reversed in alternate sheets, as can be seen in fig. 3, where the sheets are shown edge-on, and the manner in which they can slide in opposite directions about the symmetry centres, parallel to the [100] axis, becomes clear. A rough model, and diagrams made with the approximately known dimensions of the calcium atom and SO_4 group, showed the packing of such an arrangement in the unit cell to be feasible.

Fig. 2.

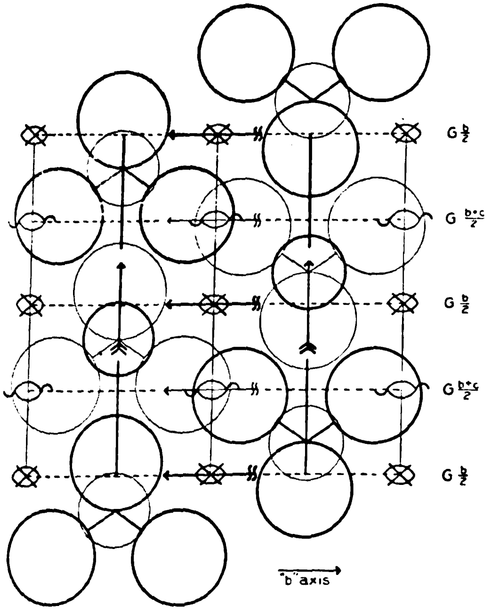


The large circles represent oxygen atoms, the small ones calcium atoms. Both are shown two-thirds their relative size compared with the unit cell. Thick circles indicate groups lying $b/2$ above those shown by thin circles.

6. *Determination of Parameters.*

Figs. 2 and 3 show that for the (010) and (001) planes, all atoms except two oxygens in each $CaSO_4$ complex lie on the X-ray reflexion planes, thus explaining the high value of the second order spectra (first observed spectra) and, since the effect of the oxygen atoms is known to fall off rapidly at higher angles, the pseudo-normal appearance of the higher orders. The interest of the reflexions from these planes lies further in the fact that the only parameter involved is the distance between oxygen centres in the SO_4 group. At first it was hoped that this would enable a comparatively accurate estimate to be made of the dimensions of the group. Owing, however, to the small percentage of the total effect contributed by the oxygens, even in the low order spectra, the calculated intensities are comparatively insensitive to variation of the parameter.

Fig. 3.



All faces in the [100] zone have intensities which depend solely on this oxygen-centre parameter, and the measured intensities from the (011) face have the additional advantage over the pinacoid reflexions that all four oxygen atoms are out of phase with the calcium and sulphur. Here also it was found that reasonable variation of the parameter gave no clear indication of its optimum value. The (022) reflexion is fairly sensitive to variation of the parameter, but again values between 2·4 and 2·5 Å seem equally satisfactory.

Table I. gives the variation in the calculated normal intensity of reflexion (ρ/S^2), for different oxygen parameters, of the various spectra from the two faces.

Table I.

Spectra.

Parameter Å	020	040	060	080	0.10.0	022	044	066
2·3	698	200	54·0	13	7	375	38·4	12·2
2·4	752	187	54·3	13	7	504	34·7	12·2
2·45	768	171	54·6	13	7	575	34·3	12·2
2·5	792	162	55·0	13	7	669	31·6	12·2
2·6	835	147	56·5	13	7	908	28·6	12·2

The distance between oxygen centres was finally taken as 2·45 Å, this giving the best concordance for all spectra considered.

The scattering power of the oxygens is so reduced in other faces of the zone by the increasing glancing angle that no conclusion can be drawn from their intensities.

Taking into account the low accuracy of the intensity measurements, it was not possible therefore to determine the distance between oxygen centres from measurements on this zone alone, without additional evidence derived from reflexions involving the two other parameters of the system.

All these parameters are most conveniently expressed, for the purpose of intensity calculations, as angular differences in phase, the dimensions of the unit cell representing phase differences of 360° in the directions of the crystal axes.

It seemed reasonable to assume as a first approximation that the calcium atoms lie half-way between two SO_4 groups, so that the two unknown parameters could not differ widely from the values n° and $(n+180)^\circ$. An important clue as to the approximate value of n is given by the strength of the (210) reflexion. This shows that the atoms must be grouped very close to these planes, and from fig. 3 this can be seen to occur when n is in the neighbourhood of -35° for calcium, giving $+145^\circ$ for sulphur, the coordinates being referred to a centre of symmetry for simplicity in calculation.

A systematic test of the assumed structure was then carried out, and the effects of variation of both parameters investigated. The method of carrying out such tests has already been described by James and Wood (*loc. cit.*) and need only be summarized here.

All observed spectra are tabulated in order of increasing glancing angle, and the observed intensities divided by the calculated intensity ratios to give the 'normal' intensity ρ_n of reflexion that would be given by all the atoms in phase at that particular angle. If the structure is correct, ρ_n diminishes rapidly and steadily with increasing angle. Any violent anomaly indicates that the structure is incorrect, but the test must be regarded at present as principally of qualitative significance.

In assigning scattering powers at different angles to the atoms, numerical values were first taken from Hartree's tables of F values *. Oxygen and sulphur were assumed to be ionized with the charges O^{-2} and S^{+6}. We experienced difficulty, as already noted by James and Wood, in obtaining agreement with observation for the higher order spectra unless the scattering power of O^{-2} is made to die away more rapidly than given by Hartree's figures. We finally used both for oxygen and sulphur the values given by James and Wood (*loc. cit.*), Hartree's values being taken for calcium only.

A few trial intensity calculations showed that the ratio ρ/ρ_n was more nearly proportional to the square of the amplitude ratio S, which was calculated in the usual way, than to S itself, indicating that anhydrite is not to be regarded as forming perfect crystals, but a mosaic. This was checked by direct calculation from the formula for the integrated reflexion

$$\rho = \frac{N^2\lambda^3}{4\mu} \cdot \frac{e^4}{m^2c^4} \cdot \frac{1+\cos^2 2\theta}{\sin 2\theta} \cdot S^2 e^{-B\sin^2\theta} \times (\Sigma F)^2, \quad (1)$$

using for the linear absorption coefficient μ the value 25·7 derived from Wingårdh's mass absorption coefficients for molybdenum radiation †, with no allowance for extinction effect or Debye factor. Thus for the (020) spectrum (ΣF) as calculated was 41·4, while the value from Hartree's curves is 59·4. If extinction and the Debye factor were taken into account the calculated value would be raised. A normal reflexion curve for various values of $\sin\theta$ was also calculated from formula (1). The calculated values, shown in the last column of Table II., agree more closely with the observed intensities than would be the case on the assumption that ρ is proportional to S.

---

* Phil. Mag. l. p. 289 (1925).

† *Zeitschr. f. Phys.* viii. p. 263 (1922).

TABLE II.

Spectrum.	Sin θ (θ=glancing angle).	$\rho \times 10^6$ $\left(\frac{E\omega}{I} \times 10^6\right)$.	$\frac{\mu+\epsilon}{\mu} \cdot \rho$.	S^2.	$\rho_n = \frac{\mu+\epsilon}{\mu} \cdot \frac{\rho}{S^2} \times 10^6$.	Theoretical value of ρ_n.
101	0·0766	?	?	0·00866	?	2450
111	0·0920	4·8	4·9	0·00296	1650	1850
002 020	0·1021	280·0	560·0	0·365	1580	1580
200	0·1143	29·0	32·0	0·0207	1550	1310
210	0·1251	170·0	279·0	0·133	2100	1080
121	0·1277	9·6	9·9	0·00232	4270	1050
022	0·1445	32·4	36·5	0·0563	647	785
202	0·1532	11·0	11·5	0·0352	327	685
220	0·1533	102·0	141·4	0·339	418	685
222	0·1841	13·4	14·1	0·0405	348	420
004 040	0·2042	90·0	121·0	0·526	230	310
400	0·2286	7·4	7·6	0·034	224	220
303	0·2298	?	?	0·0271	?	215
420	0·2502	16·0	16·9	0·274	61·7	160
402	0·2503	30·4	34·0	0·152	224	158
242	0·2554	9·0	9·3	0·0414	224	145
333	0·2760	?	?	0·0298	?	100
044	0·2890	17·8	19·0	0·524	36·3	83
006 060	0·3063	54·0	65·2	0·990	65·9	63
404	0·3064	7·4	7·7	0·345	22·3	62·5
440	0·3066	21·0	22·8	0·400	57·0	62·0
062	0·3229	27·5	30·4	0·833	36·5	50·6
600	0·3429	31·5	35·2	0·713	49·3	40·5
620	0·3676	26·0	28·6	0·723	39·5	31·6
444	0·3680	9·3	9·6	0·582	16·4	31·5
630	0·3753	?	?	0·250	?	31·0
505	0·3830	?	?	0·00203	?	28·0
363	0·3831	?	?	0·00012	?	28·0
008 080	0·4084	13·0	13·6	1·0	13·6	23·7
066	0·4335	12·2	12·7	1·0	12·7	20·6
800	0·4572	0·2	0·2	0·0298	6·7	18·4
606	0·4596	8·1	8·4	0·750	11·2	18·2
660	0·4599	12·0	12·5	0·752	16·6	18·2
555	0·4600	?	?	0·00007	?	18·2
840	0·5004	?	?	0·0302	?	16·1
804	0·5006	?	?	0·031	?	14·9
0.0.10 0.10.0	0·5105	7·0	7·2	1·0	7·2	14·0
484	0·5108	5·6	5·7	0·590	9·5	14·0
666	0·5520	2·4	2·4	0·745	3·2	11·4
10.0.0	0·5715	0·3	0·3	0·97	0·3	10·4

The intensities ρ of all observed spectra were expressed in absolute measure, taking the absolute intensity of reflexion from (400) rock-salt as 10^{-4}. ρ/S^2 gave then the value of ρ_n. Allowance for the unequal effect of extinction, which cuts down the more intense reflexions to a disproportionately large extent, was made by putting $I \propto S^2/(\mu+\epsilon)$, where the extinction factor ϵ is proportional to the intensity of reflexion I and can be written $\epsilon = \alpha I$ *. The value of α for anhydrite was deduced from the ratio of the calculated normal intensity (derived from the measured (020) intensity) to the normal intensity calculated theoretically from formula (1). All observed intensities were then multiplied by the factor $(\mu+\epsilon)/\mu$ to correct for extinction. These corrected values, divided by S^2, should form a steadily diminishing series corresponding to the theoretical intensity values, but still affected by neglect of the Debye factor.

Table II. shows our results in this form.

The parameters which gave the best agreement were calcium $-35°$ and sulphur $+145°$. These values represent displacements along the *a*-axis of $-0{\cdot}60$ and $+2{\cdot}50$ Å respectively. The degree of accuracy with which the parameters could be fixed is of the order of $\pm 0{\cdot}05$ Å. The calcium atoms appear then to be half-way between consecutive SO_4 groups on the *a*-axis, and adjacent sheets of atoms parallel to the (010) face are displaced 1·21 Å with respect to each other.

7. *Discussion of Results.*

Five of the forty-five spectra examined show considerable discrepancies in the series. These are the (101), (210), (121), (420), (630) reflexions.

From the calculated amplitude factor we should expect the (101) reflexion to have an intensity of about 20 per cent. that of (400) rock-salt, whereas its presence could not be detected at all. Moreover, this discrepancy cannot be satisfactorily overcome by any reasonable alteration in the parameters. Now the amplitude factor is quite sensitive to change in the F value for sulphur. The glancing angle is the lowest observed, and it is precisely in this region that the F value is most uncertain, and changing at its greatest rate. It would seem, at first sight, logically correct to adopt Hartree's curve for S^{+6} throughout the series. Thus, for the (101) reflexion, F would have the value 10, instead of the value 14·2 taken by us from James and Wood, and the resulting amplitude factor would be reduced from 0·0087 to 0·0024. But this change adversely affects the four or five spectra occurring at angles where the divergence of the F curves for S^{-2} and S^{+6} is still appreciable. The (111) and (121) spectra are especially sensitive to the change, the calculated normal reflexion for the latter assuming such a value as to render the change questionable.

---

* *Cf.* W. L. Bragg, Phil. Mag. l. p. 309 (1925).

Some polarization of the oxygen atoms of the SO_4 group seems likely, and it is possible that the intensity at low glancing angles is affected by the asymmetry of the oxygen electron shells.

However, we have been unable to reach a satisfactory compromise, and have preferred to retain the F values that give concordant results in other structures.

The (121) reflexion gives too high a value for ρ_n, but the low observed intensity and the sensitivity of the very small amplitude factor could easily account for this.

The three remaining discrepancies occur in reflexions of different orders from the (210) planes. As already noted, the calcium and sulphur atoms are closely concentrated near these planes, and the combined scattering power of all oxygen atoms is only one-fifth of the total effect, even in the first order. The contribution of the oxygens is, however, quite susceptible to variation in the sulphur parameter. It is in faces of this character also that small distortions of the SO_4 tetrahedra might be expected to produce considerable effect.

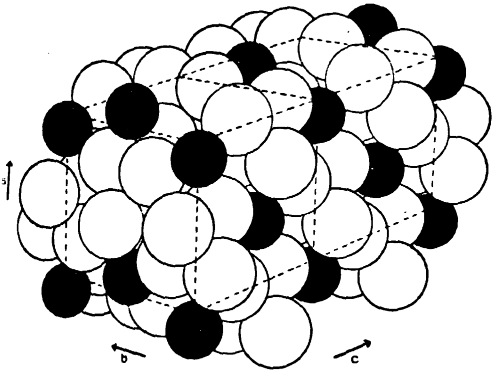
The coordinates already chosen appear to give the best general agreement when all spectra are considered.

Fig. 4 shows the structure to scale, the black spheres representing calcium ions, and the white spheres oxygen ions grouped in tetrahedra; the sulphur ions not being visible. The positions of two contiguous unit cells are indicated by dotted lines.

The *b* face of the model reveals the face-centred arrangement of the calcium atoms and SO_4 groups, whereas the *c* face shows the displacement of alternate sheets of atoms in the *a* direction.

Each calcium atom is immediately surrounded by eight oxygen atoms belonging to six tetrahedra, four of these being at a distance of 2·55 Å; two at 2·43 Å, and two at 2·47 Å. The nearest distance of approach o. calcium to oxygen has been found in other crystals to be 2·4 Å. It is clear, therefore, that the calcium atoms are surrounded as uniformly as possible by oxygen atoms, the arrangement of the oxygens in tetrahedra preventing perfect uniformity.

Fig. 4.



The smallest distance between calcium atom centres is 3·68 Å; the distance between sulphur and oxygen centres is 1·50 Å.

Summary.

The structure of anhydrite has been determined by the ionization spectrometer. It is based on a simple orthorhombic lattice, the unit cell containing four molecules. The space-group V_h^{17} previously determined by Rinne, was corroborated by the Debye powder method.

Assuming a regular tetrahedral arrangement of the SO_4 group, two parameters suffice to fix the positions of all its atoms in the unit cell. The positions of the calcium atoms involve only a single parameter.

In calculating amplitude factors, some deviations from Hartree's F values for scattering power have had to be made, as already noted by other workers.

We wish to express our thanks to Professor W. L. Bragg, F.R.S., for his help and interest in the progress of the work. We are also indebted to Mr. R. W. James for much helpful advice and criticism.

Note.

Since writing this paper we have seen a copy of a most interesting determination of the structure of anhydrite and the configuration of the SO_4 group by J. A. Wasastjerna [*], communicated to the Societas Scientiarum Fennica on Sept. 23rd, 1925.

The author shows from symmetry and intensity considerations that a tetrahedral arrangement of the SO_4 group is the only possible one, and deduces a structure from which ours differs only in the values of the parameters.

But in the theoretical calculation of reflexion intensities he states that, on empirical grounds, he considers it impossible to obtain agreement between observed and calculated intensities for anhydrite if the intensity is taken as proportional to the square of the amplitude factor (S^2), whereas he was able to get a fairly good agreement by taking the intensity as proportional to S; that is to say, treating anhydrite as an approximately perfect crystal. As shown in our paper, this does not seem to be justifiable either on a theoreticl or empirical grounds.

In calculating reflexion intensities Wasastjerna uses the formula

$$R = \frac{1}{\sin^2\theta} \Sigma \rho_m \cos 2\pi n (hx_m + ky_m + lz_m),$$

and treats the scattering power ρ_m of an atom at various glancing angles as approximately constant.

With the exception of the pinacoid reflexions, which were measured spectrometrically, his observed intensities are taken from powder photographs using copper radiation, and are merely classified into five degrees from "very strong" to "very weak."

It is interesting to note that he obtains a weak (101) reflexion.

In terms of our notation his coordinates become $Ca = -54°{\cdot}0$ $S = +126°{\cdot}0$, in place of our $Ca = -35°$ $S = +145°$.

The mean distance between oxygen centres in the SO_4 tetrahedron is 2·7 Å as against our value 2·45 Å.

Manchester University.
12th March, 1926.

---

[*] *Soc. Scient. Fenn. Comm. Phys.-Math.* ii. p. 26.

IX. *A New Method of obtaining a Luminous Discharge in Gases at very Low Pressures.* *By* E. W. B. GILL, *M.A.*, *B.Sc.*, *Fellow of Merton College, Oxford*, *and* R. H. DONALDSON, *M.A.*, *University College, Oxford* *.

(1) THE discharges in gases at low pressures obtained with alternating potentials or with high-frequency potentials, such as are obtained in ordinary oscillatory circuits, have been the subject of many investigations, but no measurements appear to have been made of the potentials required to maintain currents in gases when the frequency of the oscillatory potential is of the order of 40 million oscillations per second, which is the frequency corresponding to a wave-length of about 8 metres.

We have recently made some investigations of the currents in gases with potentials differing in frequency over a very wide range, and we find that the absolute value of the potential required to maintain a current in a gas is greatly reduced when oscillations of very short wave-lengths are used. It is difficult to measure these potentials accurately, but the effect of increasing the frequency is so marked that it is sufficient in this preliminary account of the experiments to give the values of the potentials to an accuracy of about ten per cent.

To illustrate this effect we give the results ot experiments made with hydrogen, where the potentials required to maintain a small current at different pressures were determined, (*a*) with direct voltage, (*b*) with voltages alternating about 200,000 times a second, and (*c*) with voltages alternating about 40,000,000 times a second. The last investigation revealed a simple method of obtaining a luminous discharge through a gas at a pressure of a thousandth of a millimetre of mercury, that is at a pressure considerably lower than that in an ordinary X-ray tube.

(2) The discharge-tube used was a glass cylinder about 25 cm. long and 4·5 cm. diameter. The electrodes were two brass rods of diameter 1 mm.; they were sealed into two side tubes through copper glass seals, and these side tubes were sealed into the main tube not quite opposite to each other in such a way that the brass rods were parallel and about 3 cm. apart. The actual shape of the tube is shown

---

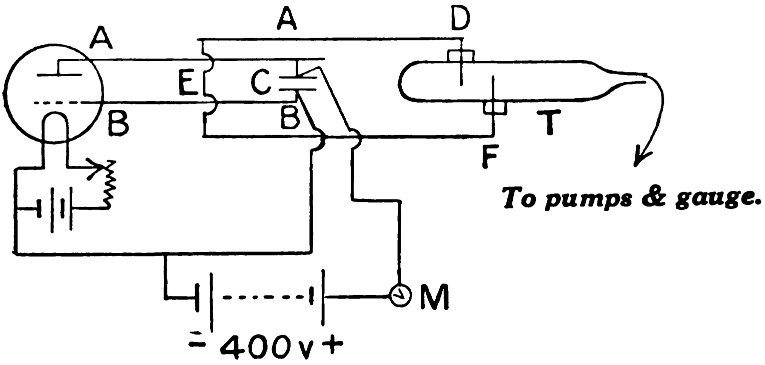
* Communicated by Prof. J. S. Townsend, M.A., F.R.S.

in fig. 1, where D and F are the two rods projecting into the main tube T.

The tube was joined up to a mercury pump. A McLeod gauge and drying tubes and a palladium tube were also inserted.

The whole apparatus was pumped out and washed out several times with hydrogen admitted through the palladium tube.

Fig. 1.



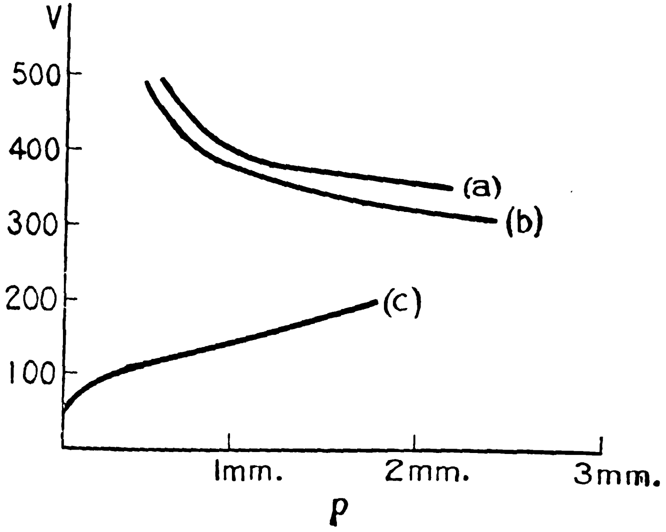
(3) The experiments to find the potentials required to maintain a small direct current through the hydrogen at various low pressures need not be described in much detail. The tube was connected to a battery of small accumulators, the current being kept as small as desired by inserting in one of the leads a small rectifying valve which would only pass a small current dependent on the temperature of the filament. The potential across the tube was read by an electrostatic voltmeter.

The results obtained are given in curve (*a*) fig. 2. The usual type of curve for maintenance potentials is one in which for high pressures the potential is very high; as the pressure is reduced, the potential also falls and reaches a minimum, and a further reduction in pressure causes the potential to rise very rapidly. It will be seen that the range of pressures worked over in curve (*a*) are below the pressure which gives the minimum potential.

(4) The next set of experiments, curve (*b*) fig. 2, were done with an alternating E.M.F. An oscillatory circuit consisting of an inductance and capacity was maintained in oscillation by a valve using the ordinary reaction circuit. The wave-length of the circuit was 1430 metres, corresponding to a

frequency of 210,000 alternations per second. The discharge-tube and the electrostatic voltmeter were both connected across the condenser. When the valve (a Mullard 0 30 A) was taking its rated filament current and 400 volts in the plate circuit, there was enough potential across the condenser to light the discharge-tube brightly at pressures of a few millimetres of mercury. The strength of the oscillations was then reduced by gradually reducing the filament current of the valve till the discharge was only just maintained.

Fig. 2.



Minimum potential V required to maintain a discharge at different pressures *p*.
(*a*) Direct current. (*b*) Current periodicity 200,000.
(*c*) Current periodicity 40,000,000.

The potentials indicated by the electrostatic voltmeter as being necessary to maintain the discharge are shown in curve (*b*). It should be noted that these potentials are not the maximum potentials across the tube as the voltmeter gives the mean square of the potential. The maximum, or "peak" value, would be obtained by multiplying the readings by $\sqrt{2}$, though this would not be quite accurate as the wave-form was not exactly that of a sine curve. The general shapes of the two curves (*a*) and (*b*) are much the same.

(5) The last set of experiments given by curve (c) fig. 2

was made with a much higher frequency, a wave-length of 8·25 metres being used corresponding to about $3·6 \times 10^7$ alternations a second.

The short-wave generator was a slight modification of the type devised by Townsend and Morrell*, and is shown in fig. 1.

AA and BB are two brass strips 13 mm. by 3 mm., each 161 cm. long, placed flat and parallel to each other, the distance between their centres being 6·5 cm. One end of AA is joined to the plate of a Mullard 0 30 A valve and one end of BB to the grid. The other ends of the strips are joined to the condenser C, which is of the order of a milli-microfarad. The plate is charged to about 400 volts positively to the filament by a lead brought into AA at the condenser end, and the grid is put at the same potential as the negative end of the filament by a similar lead to BB. It was convenient to have a milliammeter M in the plate lead.

When the valve filament is heated by a six-volt battery this set produces powerful oscillations with a wave-length of 8·25 metres. The presence of these oscillations is shown by the milliammeter M reading from 40 to 60 milliamps, whereas if the oscillations are damped by touching BB at the grid end the plate current drops to a few milliamps.

The amplitude of the oscillating current is not the same everywhere along the strips, being largest at the condenser end and smallest at the grid end.

This arrangement is so simple and convenient for short waves that a few more remarks may be of assistance. AA and BB need not be strips, ordinary wire or rod will do, and their distance apart is not important except that it should not be less than 3 or 4 cm. The size of the condenser C is not important either, provided it is not too small it will be situated at a potential node and have no effect on the wave-length. It should be noticed that it has a potential of 400 volts across it.

Any small transmitting valve dissipating about 30 watts at the plate will be suitable, but the wave-length will vary slightly with different valves. The leads from the H.T. battery and filament to the condenser ends of AA and BB should not lie too close to the strips.

As mentioned above, with strips 161 cm. long the wave-length was 8·25 metres. A rough rule is that a reduction x in the length of the strips reduces the wave-length by $4x$, so that the length of strip for any desired wave-length λ is $\frac{\lambda - 181}{4}$ cm., λ being measured in cms. The oscillations are not very powerful for wave-lengths less than 3 metres.

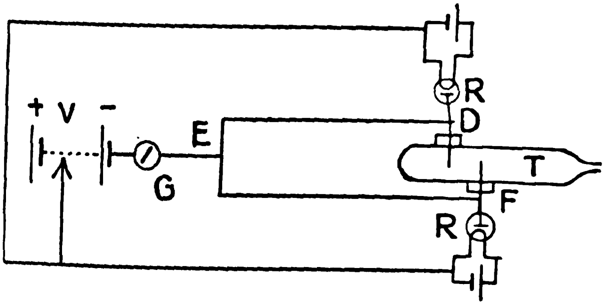
---

* Phil. Mag. August 1921.

It is not possible to put the discharge-tube directly across the oscillating system as the potential differences are scarcely large enough, and in addition the 400 volts steady potential would be superimposed upon the alternating potential. A further objection is that the capacity of the discharge-tube and the current through it would disturb the wave-length.

The tube therefore was put across a circuit DEF electromagnetically coupled to the oscillator. This circuit has a natural wave-length of about 4 times the length DE, and when it oscillates E is a potential node and the maximum potential occurs between the free ends, *i.e.* across the discharge-tube. It is not necessary to tune this circuit accurately to the wave-length of the transmitter, as sharp resonance effects are not obtained when a discharge occurs in the tube T, but it is desirable to make the length DE somewhere about $\lambda/4$. In our experiments this length was about 2 metres, and a convenient coupling was obtained when the two circuits overlapped by 60 cm., the plane of the circuit DEF being about 3 cm. above the plane AABB. If the coupling is too tight the wave-length of the transmitter will be altered, or in extreme cases the valve may not be able to produce oscillations.

Fig. 3.



The measurements of the oscillating potential across the discharge-tube presents very considerable difficulties, and the method to be described does not claim to be more than a rough one though sufficient for our purposes, as we only desired to know the general shape of the curve.

It is not possible to attach to the ends D, F any measuring device which has a capacity of more than a few electrostatic units, as the potential would be too much reduced thereby, and the method therefore finally adopted is shown in fig. 3. R, R are two small rectifying valves whose plates are joined to the secondary circuit at the same points as the discharge-tube. The negative ends of the filament batteries of these valves are joined back to the point E through a variable source of potential V and a delicate galvanometer G.

The point E is a node of potential, and if its potential is taken as zero the potential of D will be $V_0 \sin pt$ when that of F is $-V_0 \sin pt$. If V is greater than V_0 the plates of the rectifying valves must always be at a negative potential relative to their filaments, and no current can flow through the valves. If V is less than V_0 the plates are positive to the filaments once in each alternation, and currents will flow through the valves and be registered by G.

V is therefore adjusted till G just reads no current, and the value of V_0 thus found. The "peak" value of the alternating E.M.F. is $2V_0$.

Were it not for the valve capacity one valve would be sufficient, two similar valves keeps the set symmetrical.

This arrangement as already stated is not ideal. The potential measured is that just outside the discharge-tube, which is not quite the same as that between the electrodes where the discharge is occurring. There may be a small potential distribution down the leads from the filaments to E, and for the high frequency used the time the electrons take to cross the valves is for small voltages comparable to the time of oscillation, which will introduce an error not yet estimated but not more than a few volts. The method of experiment was to have the transmitter and secondary circuit coupled together, the secondary circuit having its two rectifying valve circuits attached, and the transmitting valve was then turned full on. If the tube did not light up it could generally be started by a spark from a small induction coil, one of the secondary terminals of which was joined to the node E and the other of which was placed about 1 cm. from the wire at F. The discharge was then reduced either by loosening the coupling, or reducing the filament current of the transmitting valve, or both, till the discharge was only just passing, when the peak voltage $2V_0$ was determined as above. The results for various low pressures are shown in curve (*c*) fig. 2.

For very low pressures the only way to get the discharge going was to raise the pressure slightly, start the discharge, and then, keeping the discharge running, pump down again to the lower pressure. When the discharge was going it was not possible to stop it by reducing the pressure as far as it could possibly be reduced by a Toepler pump.

(6) Curve (*c*) shows that there is a very striking difference between the conditions for the maintenance of a discharge when the applied E.M.F. alternates 36 million times a second and when it alternates 200 thousand times or is unidirectional. In the latter cases, the minimum potential for maintenance with the tube used occurs at about 3 mm. pressure, but in the former case, even when the pressure had been reduced to 1/50 mm., the minimum potential had not been reached. The difference in the magnitude of the potentials required is also remarkable; the R.M.S. of the minimum potential for the 200 thousand oscillation is about 300 volts, but with the 36 million oscillation a peak valve of 100 volts will maintain the current with pressures much smaller than that at which the ordinary minimum sparking potential is obtained.

The large effect obtained with the short-waved oscillations may be seen from the consideration that the pressure of 1/100 mm. of mercury is of the order of pressure of an X-ray bulb, and at about this pressure a discharge from an induction coil passed more easily through air at atmospheric pressure between electrodes 10 centimetres apart, in parallel with the bulb. Yet on the short wave at this pressure the tube was brightly illuminated, when the potential difference between the terminals was about 150 volts.

(7) The discharge in the bulb was obtained with pressure much less than 1/100 mm. It was found that if the discharge was left running with the gas at about 1/100 mm. pressure, the hydrogen gradually disappeared and the pressure fell till it was less than 1/1000 mm. At this very low pressure the spectrum of the discharge showed very bright mercury lines and scarcely any trace of the hydrogen spectrum. For this reason too much stress should not be laid on the actual values of the potential for current maintenance at the lowest pressures, as at these the mercury vapour appears to have more effect than the hydrogen.

It is worthy of note that at the very lowest pressure attained the potential required to maintain the discharge was only a few volts.

It was also found that the discharge was obtained at very low pressures in hydrogen from which the mercury vapour was removed by charcoal cooled with liquid air.

(8) From the spectroscopic point of view, the short-wave transmitter appears to offer the means of working at pressures considerably lower than those which hitherto have been found practicable. It is an advantage for spectroscopy to eliminate the electrodes, and some experiments were made

to see if the short wave would produce an electrodeless discharge. For this purpose the same transmitter and coupled circuits were used, except that the open ends of the secondary circuit, instead of being joined to the electrodes of the discharge-tube, were laid along the outside of the tube on opposite sides of it, or better still looped round it a few cms. apart. On starting the valve transmitter, it was found that the tube, if at a fairly low pressure, lit up at once. For the very low pressures it was necessary to help the discharge to start with an induction coil applied just as before described (one terminal joined to the potential node on the secondary circuit and the other a centimetre or two from one of the free ends). In this way the discharge could be started with the pressure as low as 1/500 mm. Generally speaking, it was easier to get the electrodeless discharge to pass than the discharge between electrodes. It need scarcely be added that if the luminous discharge alone is required it is unnecessary to have the two rectifying valves attached to the secondary circuit.

(9) The difficulty of obtaining the supply of electrons to maintain a direct current at very low pressures is that the majority of the electrons have very few collisions with gas molecules, and the general explanation of the ability of very rapidly alternating E.M.F.s to maintain a discharge at very low pressures is that in moving between the electrodes a large number of the electrons cover a distance many times greater than the distance between the electrodes, and thus the chance of a collision is very much larger than if the electrons passed straight across.

The general motion of the electrons up to the time they have a collision is a movement through a distance d in one direction followed by a movement d' in the reverse direction, this process being repeated indefinitely till an electrode is reached.

If the E.M.F. is V sin pt it is easy to see that in the cases where the velocity of the electrons happens to be zero at time $t=\frac{\pi}{2p}$, the electrons oscillate about a mean position; and in cases where the velocity is zero at time $t=0$ the electrons move across the tube with alternate accelerations and retardations without any reversal in the direction of motion. (These are the extreme cases.) The electrons whose velocity happens to be zero at times near to $\frac{\pi}{2p}$ have d' very nearly equal to d. These in one alternation cover a total distance $d+d'$, but actually only approach the electrode by the small distance $d-d'$.

It is, of course, essential that in its excursion d the electron does not encounter the electrode, which agrees with the fact that the low pressure phenomena only come into prominence for the extremely high frequencies where the distances d and d' can be proved to be much less than the distance between the electrodes for the particular electric forces which produce the discharges.

(10) It would appear from the preceding argument that the discharge might prefer a low voltage to a high one as the excursions would be smaller, and it was found possible to show this experimentally. A tube was taken 95 cm. long (in this case containing air) and the pressure brought very low by the use of charcoal and liquid air. The wires of the secondary circuit were laid alongside the tube and the whole tube lit up; but by reducing the strength of the valve oscillator it was possible to light up only a portion of the tube; not near the ends of the wires where the potential was biggest, but at points where the potential was less.

These experiments were conducted in the laboratory of Prof. Townsend, who has given us very much help and advice.

X. *Shape of Waves from Large Explosions.*

By T. Carlton Sutton, *M.Sc.*, *F.Inst. P.*[*]

Foreword.

The following consists of :—

(1) Some deductions as to the nature of waves emitted from large explosions, based on the accepted theory of Rankins, Hugoniot, and others.

(2) The application of these deductions to registrations of the recent explosion at La Courtine, especially to a photograph taken by M. Dufour[†].

In the argument that follows, the deductions (1) and their application (2) have, for the sake of interest, been developed together. The former hold good as deductions from general theory; on the other hand, although it seems appropriate and reasonable to apply them to M. Dufour's observations in the way that is here done, a full justification of any such step must necessarily await the collection of further evidence of a kind that can only be obtained by experiments on a very large scale.

---

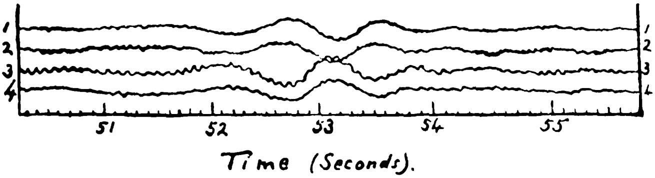
[*] Communicated by the Author.

[†] Dufour, *C. R.*, 1924.

M. Dufour's Photographs.

SOME interesting photographs have been taken by M. Dufour at the École Normale Supérieure, and give some indication of the nature of "heavy" sound waves transmitted over a long distance. The source of these waves was the explosion of a charge of 10,000 kilogrammes at La Courtine in Central France. The waves travelled about 180 miles, and were recorded at Paris by a number of Dufour microphones. These microphones consist of a large circular disk about 1 foot in diameter, carrying at the centre a small coil; when the sound impulse is received, the disks vibrate and move this coil in an intense magnetic field. In these particular measurements four microphones were used, connected with the strings of an Einthoven galvanometer in such a way that the currents passed in one direction through strings 1 and 2, and in the reverse direction through strings 3 and 4. M. Dufour's photograph is reproduced in fig. 1. The natural period of the microphone disks is of the order of 0·07 second, and is seen in the smaller fluctuations recorded; the larger fluctuations of approximately 1·0 second period are attributable to the explosion at La Courtine.

Fig. 1.



Deductions from General Theory.

M. Dufour's photograph was taken at Paris. On account of the distance (180 miles) from La Courtine, where the explosion took place, and since the nature of the ground, the cloud distribution etc., is not regular, the fluctuations registered may be due to irregular reflexion and refraction, and may represent the "drawing out" of a single wavefront.

Without considerably more evidence and measurement it is not possible to speak with any certainty; nevertheless, it is of interest to examine what shape of wave-front would be expected from a large explosion, and examination may well be made in accordance with current theory *.

This theory may be developed to show that, when explosions are sufficiently large, (1) the disturbance is of a fluctuating nature, (2) its component pulses occur in groups, separated by intervals in which no pulses occur, and (3) the number and duration of these groups increase with the size of the explosion.

That portion of the theory which affects the present issue has been summarized † :—

"When in a fluid medium, a discontinuity exists of such a nature that the pressure and density are much greater on one side of it than they are on the other side, a pulse or a series of pulses is set up which tends to decrease this difference. These pulses are pressure pulses passing from the region of high pressure into the region of low pressure, through which they will continue to travel until some other surface of discontinuity is reached or their energy becomes absorbed in the medium. They travel with a velocity greater than the velocity of the particles in the medium by an amount which is commensurate with the velocity of sound in the medium, and so of course approach and reach the boundary of the medium.

"No pulses of rarefaction originate at the discontinuity."

Consider now some phenomena of the expansion in free air of a relatively large gaseous mass produced by an explosion, taking for simplicity the hypothetical case in which the explosion is imagined instantaneous throughout the mass.

The diagrams I. to IX. (fig. 2) indicate the density distribution within the explosion gases at successive instants.

a, *b*, *c*, *d*, *e*, *f*, *g*, ... *o* represent a row of actual particles extending from the outermost layer of explosion products to the centre of the explosion. Of these, *a* at the outer edge moves outward rapidly; *b*, *c*, *d*, etc., move less rapidly; and *o* at the centre remains stationary. Consequently, the position in space of *a*, *b*, *c*, etc., varies from diagram to diagram, but the ordinate at *a*, compared with the ordinates at

---

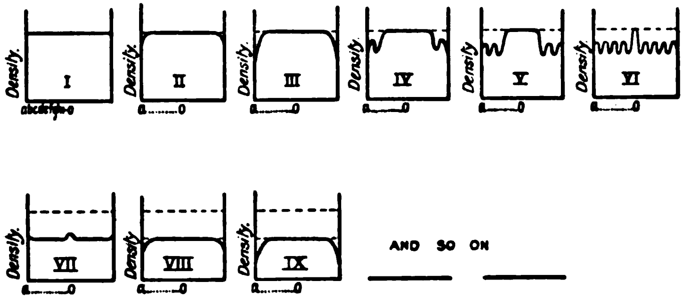
* Earnshaw, Phil. Trans. 1860. Rankin, Phil. Trans. 1870. Hugoniot, *J. de L'École Polytechnique*, 1887, 1889. Jouguet, *J. de Math. Pures et Appliqués*, 1906. Rayleigh, P. R. S. 1910. Crussard, '*La Technique Moderne*,' 1914, 1920, *et sqq*. Becker, *Z. f. Elec. Chem.* 1917.

† Jouguet, *ibid.*

b, *c*, *d*, etc., represents in each diagram the instantaneous density of the medium in the immediate neighbourhood of particle *a*, as compared with that in the immediate neighbourhood of particles *b*, *c*, *d*, etc.

Diagram I. represents the condition at, or immediately after, the explosion. In the case under consideration, conditions are then uniform for an instant, *i. e.*, pressure, temperature, density, etc., are the same throughout the exploded mass; the gradient in the interior is zero, that at the bounding surface infinite.

Fig. 2.



When conditions are as in diagram I., particles in the outer layers immediately begin to travel outwards from the centre, driving back surrounding air and mixing with it. These outer layers are the first to expand and mix, and are therefore the first to decrease in density and pressure. Towards the centre, on the other hand, the decrease is much less rapid, because (*a*) the pressure gradient, and so the outward driving force, is less in the earlier stages of the expansion, (*b*) mixing with outside air does not occur, and (*c*) loss of energy by radiation is less. That is to say, a large and increasing drop in density takes place within the medium but in its outer layers; the density of the inner layers remains high in comparison. This is indicated in diagrams II. and III.

Consequently, in addition to the discontinuity at the outer surface, steep density-gradients tend to form within the medium, and increase in steepness until something approaching a second discontinuity is attained.

Such gradients (continuous although steep) have not, as yet, yielded to mathematical analysis. The steeper the gradient, however, the more nearly it resembles the fully analysed case of a "discontinuous bounding surface of infinite gradient." If (and when) the gradient in this critical steep region becomes sufficient, a pressure pulse * is formed and passes outward through the explosion gases towards the bounding surfaces and the regions of lower pressure (diagram IV.).

The gradient is thus relieved, so that the neighbouring region towards the centre becomes the region of maximum gradient.

As the expansion continues, the gradients further increase, and a second pulse originates a finite distance within the bounding layer (diagram V.).

Similarly, subsequent pulses originate further and further from the boundary, the position of the successive surfaces at which they form passing towards the centre. Diagrams IV. to VI. indicate these phases of the pressure-distribution.

In general, this formation of pulses continues until the converging spherical surfaces of formation extend to the original centre of explosion, where they contract to a point. In this respect the pressure distribution has become that shown in diagram VI. The energy of the central region of higher pressure has now been expended, and the production of pulses ceases. As the last pulses pass outwards the distribution in diagram VII. is attained.

When relatively small masses of explosives are detonated, substantially the whole of the energy of detonation has been dissipated by the time this stage is reached.

If, however, sufficient energy remains, the conditions in diagram VII. are similar to those in diagram I., and are favourable to the production of a further series of pressure-pulses in the medium. If the size of the explosion is sufficiently large, phases II. to VI. may therefore be repeated time after time and series after series of pulses be formed.

Within the mass of explosion products, therefore, there may originate a number of series of pressure-pulses passing outwards, separated by periods during which no such pulses pass.†

Whenever a new series of pulses reaches the expanding boundary between products and air, the fall of pressure at the bounding surface is momentarily checked (may even

---

* Such pulses are additional to any which are formed at that "outer" discontinuity which necessarily exists where the outermost layer of the explosion gases is pressing against the external air.

† In explosions of small or of moderate size, only one such series forms. In larger explosions, several series may form.

be converted momentarily into a rise). The pressure between products and air therefore fluctuates in period with the arrival of each series of pulses.

In a sufficiently large explosion, therefore, the wave impressed upon the outside air is also fluctuating. It consists of a main pressure-pulse and a number of smaller superimposed pulses which themselves occur in groups and are related to the several series of pulses discussed above.

The size, period, and general nature of each such series depend on the conditions of the explosion products at the time of origin of the series. Such relation as may exist between the periods of the various series will not be a simple one, and it would be better to use observations of these periods to determine the condition of the explosion products, rather than to argue in the reverse order.

Application to M. Dufour's Photograph.

The e.m.f. induced in a magnetic coil attached to a drum diaphragm, such as was used by M. Dufour, records directly the rate of increase or decrease in pressure of the superincumbent air. A fluctuating series of groups of pulses causes, therefore, a record in which the trace passes alternately above and below the zero position, according as the pressure is momentarily increasing or decreasing.

M. Dufour's photograph is of this nature.

The simple theory developed above cannot rightly be applied unless the explosion occurs (1) in free air, and (2) at the same instant throughout the whole mass. Neither of these conditions applies to the explosion at La Courtine. The full theory will necessarily be more complex. This theory will, however, involve the production of series of pulses as in the case of the simple theory, and the chief features of M. Dufour's photograph may perhaps be interpreted on these lines rather than as the result of a mere "drawing out" of a single wave-front by refraction and by reflexions from earth and clouds. If this can be done, it would follow that :—

(i.) The groups of pulses received at Paris were of recordable magnitude for at least five seconds and were of a composite nature.

(ii.) During this time the disturbance travelled at least one mile ; the wave-front, therefore, was at least one mile in thickness.

(iii.) The gradients within the expanding explosion gases, and between them and the surrounding air, were appreciable for five seconds.

(iv.) At least five series of pressure-pulses were formed in the explosion gases during this time.

(v.) The time between the passage of the first and that of the second series of pulses (1·5 secs.) was considerably greater than the time between the passages of subsequent series (less than 1·0 sec.).

(vi.) The rate of change of pressure on the microphones (*i.e.* the suddenness with which pulses were produced in the explosion gases) was greatest for the second and third series.

Variation with Size of Explosion.

The time occupied in the formation of a series of pulses in the way described above, depends upon the time taken by the converging spherical surfaces (of steep gradient) to pass to the centre of explosion. In general, the greater the volume of explosive detonated the longer the path to be traversed by these surfaces, and consequently the longer the recorded pulses.

M. Villard * and M. Dufour have noted this from the experimental side. By examining a large number of sound-ranging records they have traced this relation between "size of gun and duration of the wave emitted" (measured by the time during which the strings of an Einthoven galvanometer remain deflected), and found that the duration of the wave increased with the mass of explosive fired. The prolonged deflexions in the case of the explosion of 10,000 kilogrammes at La Courtine confirms this relation.

A more detailed analysis of this matter is scarcely warranted at present; those remarks are confined, therefore, to indicating how this interesting and remarkable record may be interpreted in accordance with the demands of current theory.

My thanks are due to the Director of Artillery for authority to publish.

Research Department,
Woolwich.

---

* Villard, *Comptes Rendus*, 1924.

XI. *The Transmission of Sound through the Head. By* H. BANISTER, *B.Sc.* (*Lond.*), *Ph.D.* (*Cantab.*), *St. John's College, Cambridge* *.

I. Introduction .... paras. 1–7
II. Purpose of the Paper .... para. 8
III. Previous Work .... paras. 9–21
  (*a*) Cappivaccius (1509) & Mach (1874) .... para. 9
  (*b*) Thompson (1877) .... para. 10
  (*c*) Hermann (1891) and Foster (1891) .... para. 11
  (*d*) Cross & Godwin (1891) ...... para. 12
  (*e*) Mader (1900) .... paras. 13–15
  (*f*) Rostosky (1902) .... para. 16
  (*g*) Myers & Wilson (1908) ...... paras. 17–18
  (*h*) Nikiforowsky (1912) .... para. 19
  (*i*) Peterson (1916) .... para. 20
  (*j*) Stewart (1917, 1920, 1922) .. para. 21
IV. Remarks on this Work .... paras. 22–24
V. My Experiments .... paras. 25–40
  (A) Direct observation of Sound transmitted through the Head.
    (*a*) Experiment and Results .... paras. 26–28
    (*b*) Conclusions .... para. 29
  (B) Difference Tone Experiment.. paras. 30–40
    (*a*) Apparatus................ paras. 31–33
    (*b*) Method of Experiment .... para. 34
    (*c*) Experimental Results ...... paras. 35, 36
    (*d*) Conclusions .... paras. 37–40
  (C) Remarks .... paras. 41–43
VI. Summary .... paras. 44, 45

I. INTRODUCTION.

1. THE transmission of sound from one ear to the other through the head has long been a matter of interest to scientists. Not only is it important from the point of view of the general theory of hearing, but also many investigators have suggested that transmission, by way of the bones of the head, is a factor which assists in the localization of sounds.

2. In spite of its importance very little experimental work appears to have been done on the problem, neither, so far as I know, has it ever been clearly formulated.

3. A similar problem has confronted architects and builders, who have been called upon to construct sound-proof rooms; and it is only recently, chiefly within the

---

* Communicated by the Author. This research was carried out in the Psychological Laboratory, Cambridge, with the aid of a grant from the Medical Research Council.

last ten years, according to Watson [*] that the question of the transmission of sounds through buildings has been scientifically investigated.

4. In his monograph on "Sound Proof Partitions" Watson points out that two types of transmission must be discriminated. In the first type the sounding body is directly in contact with the framework of the building: in the second it is not. With the former the building itself is put into vibration, and the sounds are conducted to great distances; with the latter the sounding body sets up vibration *in the air* of the room in which it is situated. These aerial vibrations travel to the boundaries of the room, and may be transmitted to the other side through the partitions.

5. Transmission of the second type (aerial sound-waves) may take place, Watson maintains, in three ways:—(*a*) Firstly, through narrow cracks or holes, which form continuous air channels, along which the waves can percolate to the other side. This is the most common form of transmission. Sound-waves can, in this way, pass through considerable thicknesses of hair, felt, and flannel. (*b*) Secondly, the aerial waves may set the partition, or some part of it, into vibration. The partition then transmits the vibrations to the other side, setting up sound-waves on the further side as a telephone diaphragm might. With ordinary rigid walls such transmission is very slight. (*c*) Thirdly, the aerial waves may arouse elastic waves in the solid structures of the partition—waves of the same nature as those set up in the framework of the building when the vibrating body is itself in contact with the framework. The amount of this transmission is practically infinitesimal, not because the walls will not transmit such sound-waves, but because of the great difficulty in initiating them. Aerial sound-waves, even of great loudness, have comparatively little energy. The amplitude of the aerial vibration of a loud sound is, according to Shaw [†], of the order of ·004 in. So that it would be surprising if the light air particles, vibrating with so small an amplitude, had any appreciable effect on the heavy, rigidly held, particles of a wall.

6. As with buildings, so also when considering the transmission of sound energy through the head, we must clearly

---

[*] Univ. of Illinois; Eng. Expt. Station Bull. No. 127, pp. 1–78 (1922); Engineering, 114, pp. 196–197 (1922).

[†] Proc. Roy. Soc. A, lxxvi. pp. 360–366 (1905).

discriminate between (*a*) vibrations set up in the framework, the bones, etc., by direct contact with the sounding body, and transmitted to the ears by what may properly be termed "Bone-conduction"; and (*b*) vibrations due to the arrival of aerial sound-waves at the ears. It is with the latter type of transmission that we have to deal. With the former we have little concern in ordinary life, since sounds usually reach our ears as aerial waves.

7. Aerial sound-waves, falling on one ear in the usual manner through the meatus, may conceivably be transmitted through the head so as to affect the other ear in three ways:—

(*a*) The vibrating tympanum may set the air in the middle ear at the near side into vibration, and these aerial waves may pass through the sinuses or air passages to the far ear.

(*b*) The head may be made to vibrate as though it were a diaphragm, *cf.* para. 5 (*b*), when the far tympanum, in contact with the relatively stationary air on that side, would be set into motion.

(*c*) Elastic waves may be set up in the framework of the head and thus transmitted to the far ear.

It seems probable, however, that any transmission which may occur, with sounds of ordinary intensity, is due either to (*a*) air transmission through the sinuses, or (*c*) elastic waves of some nature in the head itself.

II. PURPOSE OF THE PAPER.

8. The purpose of this paper is to make a preliminary survey of the evidence for the assumption that air-borne sounds communicated to one ear in the normal manner can be transmitted through the head to the other ear; and if so, to consider the further question of the details of such transmission, *e.g.*, the magnitude and the manner of the transmission.

III. PREVIOUS WORK.

9. I am unable to find who first observed the fact that, if sound-waves are set up in the bony framework of the skull—*e.g.*, by pressing the butt of a vibrating tuning-fork against the teeth or the mastoid process—such vibrations can be heard; but Cappivaccius is stated to have ascribed

great diagnostic value to bone-conduction as early as 1509*, while it is over fifty years since Mach † (1874), suggested that the phenomenon of binaural beats might be explained by assuming that the sound was conducted from one ear to the other through the bones of the head.

10. Thompson ‡ considered the possibility of such an hypothesis in 1877, three years after Mach's suggestion, of which he does not appear to have been aware; but he dismissed it because, he argued, if the amount of bone-conduction were sufficient to account for the phenomenon of binaural beats, "There would be no reason why combinational tones should not be equally audible in binaural as in monaural audition."

11. Hermann §, 1891, also invoked the aid of bone-conduction; while Foster ‖, in the same year, after quoting an experiment which proved that sound vibrations set up in the skull are transmitted to the stapes, proceeds as follows:—

> "Not only may vibrations be transmitted from the skull to the tympanic membrane, but also conversely the vibrations of the membrane brought about in the usual way through the meatus, may be transmitted to the bones of the skull. If a long tube introduced into one meatus be spoken or sung into, the sounds may be heard by help of a stethoscope placed over various parts of the head. They are heard best perhaps at the opposite meatus; the vibrations of the bones of the skull set going by one tympanic membrane throw the other tympanic membrane also into vibration."

The experimental fact, that a sound introduced into one ear was heard through a stethoscope placed over various parts of the head, is of great interest. It is the first piece of experimental evidence, of which I am aware, to show that air-borne sounds can be transmitted through the head. We are not concerned with the speciousness of the argument which extracts from the fact the deduction, that the vibrations of the tympanic membrane are transmitted to the bones of the skull.

12. Then Cross and Goodwin ¶, in 1891, published the

---

* 'Die Krankheitendes Gehororgans,' 1827.

† Quoted by Cross & Godwin, Amer. Acad. Arts & Science, (N.S.) xix. pp. 1-12 (1891).

‡ Phil. Mag. [5] iv. p. 27 (1877).

§ Pfluger's *Archiv*, xlix. pp. 499-518 (1891).

‖ Text Book of Physiology, 1891, p. 1332.

¶ Amer. Acad. Arts & Sci., (N.S.) xix. pp. 1-12 (1891).

results of a very careful investigation they had completed, on the lines indicated by Thompson. They argued that difference tones should be heard when suitable sounds were led to the ears separately and simultaneously, if sound energy is conducted through the head to any appreciable extent. Tones were produced and conducted to the ears in various ways, viz., telephones on both ears; a telephone at one ear and a fork at the other; through tubes; and by metal rods, the tones being generated by pressing the stems of forks against the rods. In none of these experiments, when the ears were stimulated separately by tones of different pitch, could difference tones be heard, whether the sounds were quiet or deafening; but if the sound-waves were allowed to mix before reaching the ear, or if vibrations were set up in the bones of the head by putting the tuning-fork (in their second method) or one of the metal rods (in the last method) "against the head or, better, against the teeth, a loud differential tone was heard at once in the ear," which was being stimulated by aerial sound-waves.

Their conclusion was (p. 11):

> "If there were any material bone-conduction, it certainly seems as if the very loud sounds used by us would have given evidence of it at least by the occasional production of differential tones when the sounds actuated separate ears."

13. Mader *, in 1900, carried out a long series of experiments on human heads, one of which had the top of the skull and the brain removed, while another was whole. The heads were preserved in formalin. In some of his experiments sounds were led sometimes to one ear only, and sometimes to both ears simultaneously, through rubber tubes, the ends of which were either inserted into, or fixed very close to, the meatus. A specially constructed microphone, with a needle attached to one plate, was used for detecting vibrations in selected parts of the bones of the heads. The needle was placed against the bone under examination, the fleshy covering of the bone being removed to ensure good contact. The microphone was connected to a telephone in an adjoining room, where the observer sat.

14. Mader states (p. 47) that he tested the microphone in each experiment, and that, though it was very sensitive, in none of the observations he publishes was there any trace of the sound-waves acting directly on the microphone.

---

* *Sitzungsber d. Kais. Akad. d. Wissens. Wien*, cix. pp. 77-35 (1900).

15. He found unmistakable evidence of vibrations in the microphone when sounds were led into or close to the ears, and concluded that air-borne waves could induce vibrations in the bones of the skull. His view was (p. 67) that the waves of compression and rarefaction in the air in the meatus and in the middle ear "produce sound-waves in the surrounding masses of bone."

16. Rostosky[*], 1902, seven years later, put forward an hypothesis, to explain the phenomena of binaural beats, which was almost identical with that suggested, apparently quite independently, by Myers and Wilson in 1908 as a possible explanation of the "phase effect". Rostosky showed how, by assuming "bone conduction", the phenomena of binaural beats could be explained. But, as Stewart pointed out in 1917[†], Rostosky made a mistake of a sign, so that, according to his theory, the sound would be localized on the right when it was actually on the left, an error which Myers and Wilson avoided.

17. When Myers and Wilson[‡], 1908, proposed their hypothesis of the localization of tones by binaural differences of phase, they justified the assumption that sound entering one ear is transmitted through the bone of the head to the internal ear on the opposite side on these grounds[§]:

> "It is impossible to stimulate the end organs of one ear without at the same time stimulating those of the other ear. When a sound is led to one ear, not only does it pass to the cochlea of that ear but, traversing the bony vault and base of the skull, it also travels to the opposite internal ear. . . . . . . One is apt to neglect this bone conduction of sound from ear to ear, under conditions when two tones are led by tubes from separate rooms, one tone to each ear of the observer who sits in an intermediate room. . . . . Yet there cannot be the slightest doubt, even under these circumstances, as to the transference of each tone by bone conduction of the opposite ear."

18. In support of this statement they quote Mader's experiments and an experiment they themselves performed,

---

[*] Philos. Stud. xix. pp. 557-598 (1902).

[†] Phys. Rev. ix. p. 517 (1917).

[‡] Proc. Roy. Soc. lxxx. A, pp. 260-266 (1908); Brit. Journ. Psych. ii. pp. 363-385 (1908).

[§] Brit. Journ. Psych. ii. p. 380 (1908).

which is similar to the one described by Foster. Myers and Wilson give this account of their experiment * :—

> "It was found that an appreciable amount of sound could be sent through a person's head from one ear to the other. Ear caps with tubes attached were fitted to each ear, and a vibrating tuning-fork was held near the end of one tube. An observer listened at the end of the other tube, and with a fork of frequency 512 a distinct sound was heard, which *seemed to come* along the tube, [My italics.] The amount of sound getting through the head must, of course, be much smaller than the amount entering one ear and getting to the opposite internal ear."

In another paper † what is apparently the same experiment is thus described :—

> "We ourselves, by leading the tone of a tuning-fork to one ear of an individual, proved that an appreciable amount of sound could be transmitted through his head to the other ear and could thence be conducted by a tube so as to be audible to the ears of a second observer."

19. In 1912, Nikiforowsky ‡ endeavoured to obtain experimental evidence of the transmission of sound through the head. He employed a specially constructed microphone, isolated in lead, to detect sound vibrations under three different conditions.

(*a*) When the sound was produced by the subject speaking or singing ;
(*b*) When the sounding body, *e.g.* a tuning-fork, was outside the subject's body, but was in direct contact with the head ;
(*c*) When aerial sound-waves impinged on the head.

His results showed that, with (*a*), the flow of energy is greatest through the nose and mouth and that "the quantity of energy flowing from the ears is relatively large" (p. 196), while comparatively little energy flows from the hard parts of the head ;

With (*b*), "the hard parts of the head propagate the sound better than the soft, and the sound energy flowing from the ears exceeds, under the same conditions, that from the other parts of the head" (p. 197).

---

* Proc. Roy. Soc. lxxx. A, p. 266 (1908).
† Brit. Journ. Psych. ii. p. 381 (1908).
‡ *Zeit. f. Sinnes Physiol.* xlvi. pp. 179-192 (1912).

With (*c*), in spite of "very numerous and diverse experiments" with sounds "as strong as possible" he could obtain nothing positive, and concluded that the amount of sound which could penetrate inside the head was exceedingly small.

20. Peterson *, carried out an inquiry into "The Nature and Probable Origin of Binaural Beats" in 1916, and also included in his investigation an extensive series of experiments on an observer who was deaf in one ear. By no method could he obtain any evidence that aerial sound-waves, impinging on one ear, could excite the other ear also. He states his conclusions thus (p. 349):—

> "Binaural beats and the perception of phase differences [cannot] be explained on the basis of conduction of the sound wave from ear to ear through the skull. . . . . Both of these phenomena seem to be cortical in origin, while monaural beats probably originate in the basilar membrane. Combination tones, both subjective and objective, are in all probability objective in origin to the basilar membrane."

21. Stewart (1917, 1920, and 1922), while maintaining that bone-conduction cannot be a possible explanation of the general phenomena of binaural beats or lie at the basis of our perception of phase †, nevertheless falls back on such transmission as an explanation of the maxima and minima of intensities he perceived in binaural beats ‡.

IV. Remarks on this Work.

22. The only direct evidence I have been able to discover, which is adduced as proof of the transmission of aerial-bone sound-waves through the head, is contained in the experiments described by (*a*) Foster (para. 11); (*b*) Mader (paras. 13–15); and (*c*) Myers and Wilson (paras. 17, 18).

23. Mader's evidence is very direct and emphatic. The account he gives of his experiments leaves little room to doubt his observations. He was, admittedly, working with dead heads; but, if sound-waves can be set up in the bones of a dead head by aerial vibrations led into the ears, there is every possibility that they can similarly be produced in the bones of the living head. Against this evidence, however, we must set that of Nikiforowsky, whose results

---

* Psych. Rev. xxiii. pp. 333–351 (1916).

† Phys. Rev. xv. pp. 425–445 (1920).

‡ Psych. Monog. xxv. pp. 31–46 (1917–18); Phys. Rev. ix. pp. 502–528 (1917).

were negative. Nikiforowsky worked with the living head, and with a microphone which was carefully shielded from air-borne sound-waves, which Mader's was not. The experiment should be repeated, preferably by a psychologist. With the powerful means of attack which are now available, it should be possible to obtain data which will either prove or refute Mader's results. I hope to carry out such an investigation in the near future.

24. As regards Myers and Wilson's experiment, the lack of details of the measures taken to prevent the sound from reaching their observer by ordinary air paths makes one hesitate to accept the observations as proof that "an appreciable amount of sound could be transmitted through" an individual's head. Their observations, and the similar ones by Foster, require confirmation; especially in view of the evidence produced by Peterson that he could not make his monaural subject hear a note led to his deaf ear when the normal ear was plugged. If the deductions drawn by Foster and by Myers and Wilson from their observations are correct, that is if the sounds heard by them had actually travelled through the head of their subject, it is difficult to understand why Peterson's monaural subject could not hear a sound introduced into his deaf ear.

V. MY EXPERIMENTS.

25. I have accordingly repeated the observations of Foster and of Myers and Wilson, with the modifications I indicate later. I have also repeated the experiment of Cross and Godwin, to see if I could find any evidence for the transmission of sounds through the head by the detection of difference tones when the primary tones were led separately and simultaneously to the ears.

(A) *Direct observation of Sound transmitted through the Head.*

(a) *Experiment and Results.*

26. I at first attempted to repeat Foster's experiment, the subject and observer being together in the sound-proof room.

The sound was produced by a telephone at the subject's ear. I endeavoured to isolate the sound, so that it could not be heard by another person in the sound-proof room. In this I was quite unsuccessful with the means at my disposal, unless I made the sound very quiet. This would obviously make it very difficult to detect the sound, after transmission through the head. I therefore turned my attention to the observer. He was provided with an ordinary stethoscope, as in the experiment described by Foster, with which he explored the subject's head. Preliminary experiments showed that the observer was by no means isolated from sound. Even when he pressed the mouth of the stethoscope firmly against the fleshy part of his thumb, he could still hear the subject speak, and he could still hear a vibrating tuning-fork or telephone held in the subject's hand, though the loudness was considerably decreased. If the subject held the vibrating tuning-fork or telephone near one ear, the observer could clearly hear the note when he held the stethoscope near to, or touching, the subject's head. If the observer now placed the stethoscope receiver against the subject's head the loudness of the sound decreased, and at times could not be heard at all, if the rim of the receiver made good contact all round its circumference with the head. This decrease in loudness was observed whatever the part of the head to which the stethoscope receiver was applied, provided the contact between the receiver and the head was sufficiently good.

27. The experiment was now repeated under conditions which, without any doubt, gave rise to bone-conduction. Bone-conduction was obtained by the subject holding a gently vibrating tuning-fork between his teeth. With the receiver of the stethoscope near the head, the observer either could not hear the fork at all or else he heard it but faintly; with the stethoscope receiver in contact with the head the sound became much louder, while, if the receiver were pressed on a bone, the fork was heard very distinctly and could be heard sometimes even after the subject had ceased to hear it. This depended, apparently, on the relative auditory acuity of the subject and of the observer.

28. It might be argued that these experimental results can be explained as follows. The pressure of the mouth of the stethoscope in the first experiment prevents the bone from vibrating, and so the sound grows quieter as the pressure increases: in the second experiment the osseous vibrations are so great that they are not damped by the pressure. This explanation is not, I think, very probable In the first experiment the loudness of the sound heard by the observer decreased very perceptibly whenever there was good contact between the stethoscope receiver and the head. Pressure was only necessary when good contact was otherwise impossible owing to the unevenness of the surface. In the second experiment the sound of the tuning-fork held

between the teeth could be heard, when the stethoscope was pressed against the mastoid process. Sometimes the sound could be heard by the observer for a longer time than the subject himself could hear it, that is when the amplitude of the osseous vibrations was too small for the subject to appreciate the sound.

(b) *Conclusion.*

29. These experiments would seem therefore to support Nikiforowsky's finding, and to throw doubt on the validity of Foster's and of Myers and Wilson's deductions, (*a*) that aerial sound-waves of ordinary intensity can be transmitted through the head so as to be heard on the other side, and (*b*) that the transmission is due to bone-conduction. No matter how the sounds reached their observers it would seem clear that they were not transmitted by bone-conduction.

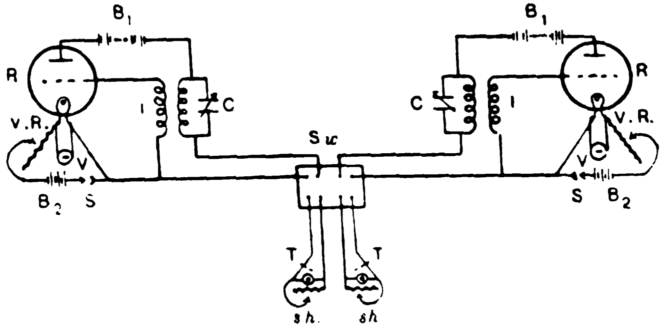
(B) *Difference Tone Experiment.*

30. My Difference Tone Experiment is a repetition of that performed by Cross and Godwin. The only variation is in the apparatus used.

(a) *Apparatus.*

31. The tones were produced by telephones in oscillating circuits *, as shown diagrammatically in fig. 1.

Fig. 1.—Diagram of Apparatus.



B_1. High Potential Battery (54 volts). B_2. Accumulator (6 volts) C. Variable Condenser. I. Inductances. R. Valve. S. Switch *sh.* Shunt. T. Telephone. V. Voltmeter. V.R. Variable Resistance. S*w*. 4-way Switch, by means of which the telephones can be connected to either circuit.

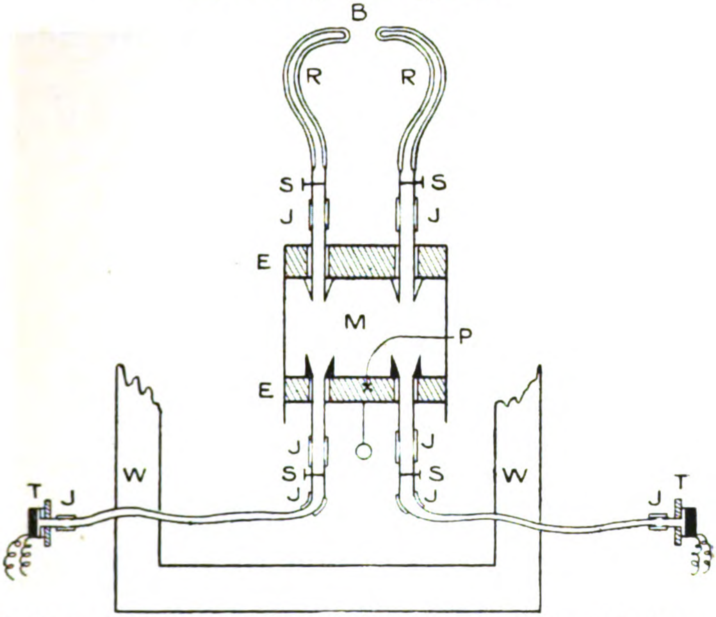
---

* A full description of the apparatus will be found in the British Journ. Psychology, xv. pp. 280–307 (1925). I am indebted to Prof. E. V. Appleton for the suggestion to use this apparatus in experiments on sound.

32. The two circuits were screened from one another by placing the one circuit into a galvanized iron cylinder. The cylinder, which is about 85 cm. long and 48 cm. in diameter (external measurements), has a double wall of galvanized iron about 2 mm. in thickness, with one thickness of iron at its base. It has no top *.

33. The sounds from the telephones were led, through metal composition tubing, into the sound-proof room, fig. 2.

Fig. 2.—Diagram of Apparatus.



B. Binaurals. E. Ebonite. J. Rubber joints strengthened by insulation tape. M. Mixing Chamber. S. Stop-cock. P. Movable Piston. T. Telephone. R. Rubber tubing. W. Walls of Sound-proof Room.

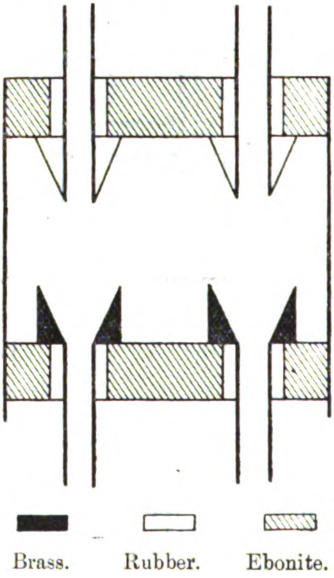
---

* (1) From the observations of Smith-Rose, Proc. Phys. Soc. xxxiv. pp. 127-138 (1922), I anticipated that there would be difficulty in screening the circuits. I found no trace of interaction between the circuits which were in separate rooms on either side of the sound-proof room, at a distance of about 4·5 metres apart. The inductances were in approximately the same plane, and the axis of the cylinder, in which one oscillating set was enclosed, was at right angles to this plane. I made no investigation of the amount of screening effected.

(2) I found that the circuit in the iron cylinder gave a note of the frequency of the oscillations, even if no telephone was in the circuit. This effect may be similar to that pointed out by Köhler, that if an oscillating current of sufficient strength is transmitted through an ordinary telephone circuit a note of the frequency of the oscillating current may be heard even if the telephone diaphragm is removed.

The tubing was joined to short brass tubes, which fitted tightly into the holes in the ebonite telephone ear-pieces, by stout rubber tubing, strengthened by a wrapping of insulation tape. The metal parts were put into as close contact as was possible. All joints were made in this manner. Stop-cocks were fixed at the ends of the tubing, so that the sounds could be cut off before reaching the mixing chamber; the sounds could also be cut off from both or either of the tubes leading to the specially constructed stethoscope binaurals, by closing the stop-cocks on the further side. The mixing chamber, fig. 3, consisted of a brass cylinder about 11 cm. long and 11 cm. in diameter. The one end was permanently closed with an ebonite plate through which two brass tubes, embedded in rubber, projected; the other end was fitted with an ebonite piston, which also carried two tubes, embedded in rubber. The whole was very accurately made and the piston had a guiding groove, to ensure that the brass tubes it carried fitted exactly over the tubes in the base. The ends of these brass tubes were bevelled and the inner ones were covered with rubber so that the joints, when the pistons were pushed home, were air-tight.

Fig. 3.—The Mixing Chamber.



(b) ***Method of Experiment.***

34. When experimenting, the observer sat in the sound-proof room with his back to the table on to which the "mixing chamber" was screwed. The experimenter stood at the other side of the table and, by moving the piston, and opening or closing one or other of the taps he could present (1) either sound to one or to both ears; or (2) the two sounds separately, one to each ear; or (3) the two sounds, mixed together, to both ears, or to one ear only (*vide* fig. 4).

Fig. 4.

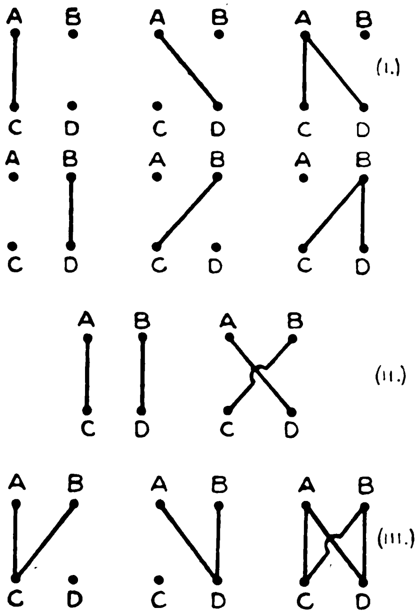


Diagram showing the possible ways in which the sounds (A, B) could be presented to the observer's ears (C, D).

The tones used had frequencies of 879 and 763 d.v./sec. so the first difference tone was a low note of 116 d.v./sec. Observers were first given the two notes separately, and were then told that they would be given the two notes together, and that they must listen particularly for the difference tone, the pitch of which was sung. When this had been recognized the experiment began. The tones were either presented separately to each ear, or were mixed in the mixer before reaching the ears, and the observer simply reported whether the difference tone was discerned or not.

(c) *Experimental Results.*

35. Five subjects were experimented on, and various other observers were tried to see if anyone could be found who could hear the difference tone when the tones were led separately to the ears. No such individual was discovered, even though the sounds were made so loud as to be uncomfortable. But if one of the binaurals was removed, and, instead, a feebly vibrating tuning-fork was held with its stem between the teeth or pressed against the bony framework of the head while an appropriate tone was led to the ear through the remaining binaural, a difference tone was clearly discriminated at the ear in which the binaural was.

36. Later I substituted a brass stop-cock, fig. 5, for the mixing chamber, so that, when the cock was closed, the two trains of waves were separated by the brass of the stop-cock and two very thin layers of vaseline, used for lubrication purposes, on each side of the brass. If aerial sound-waves are to be assumed capable of exciting vibrations in the bony framework of the skull and of thus being communicated to the other ear—which appears to be the view of Mader—"*a fortiori*" must they be conducted through the brass *.

Fig. 5.

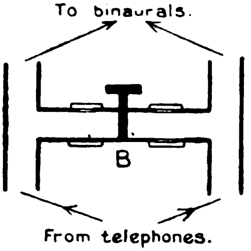


Diagram showing the brass Stop-cock (B) which was substituted for the Mixing Chamber, *vide* fig. 2.

---

* Recent experiments by Hahnemann, Hecht, and Lichte (*Zeit. Techn. Physik*, iv. pp. 93–99, 1923, have demonstrated the enormous difficulty with which sound-waves in the air can set up vibrations in a contiguous solid, and vice versa. Even with such an ideal substance as water, these experimenters found that only one-thousandth of the energy could, under the most favourable conditions, be transmitted from water to air or from air to water.

But no difference tone could be heard if the stop-cock in the connecting tube were closed. If, however, the cock were opened, ever so little, the difference tone immediately sprang into evidence. No quantitative measurements of the intensities were made, but, subjectively judged, a weak sound mixed with a much louder sound gave an easily discernible difference tone.

(d) *Conclusions.*

37. These experiments bear out fully the observations of Thompson, Cross and Godwin, and Peterson. Difference tones could not be heard when notes of suitable frequencies were led to the ears separately and simultaneously.

38. The conclusions to be drawn will depend on the theory of hearing to which one subscribes.

39. Difference tones will be produced when an asymmetrical system is subjected to two impressed harmonic forces. Such an asymmetrical system exists in the tympanum, which, according to one school, creates the difference tones normally heard when two notes of suitable frequencies and intensities are sounded. Adherents of this school would probably agree (*a*) that the experiment shows that the far tympanum was not set into vibration by sounds which had been transmitted through the head; (*b*) but that it by no means rules out the possibility of sounds being transmitted through the head from one ear to the cochlea on the other side. Another school, which might postulate the cochlea as a possible seat for the production of difference tones, would consider the evidence of this experiment as being more antagonistic still to any hypothesis of the transmission of sound through the head.

40. Adopting the point of view of the former school, it might be argued that Myers and Wilson, *cf.* paras. 17, 18, stated the necessity for bone-conduction over strongly; that it would be more correct to say that some sound is conducted through the head, but that the amount is relatively small, and that in consequence the difference tone produced at the tympanum is so weak that it cannot be appreciated.

(C) *Remarks.*

41. Wegel and Lane*, in an account of experiments published in 1924, give data which are of interest to us

---

* Phys. Rev. xxiii. pp. 266–285 (1924).

from the point of view of the transmission of sound through the head. They found that, if two tones were introduced into the same ear, and if the "pressure"[*] of the one tone was increased, a certain "pressure" would prevent the second tone from being heard. If now the tones were led separately, one to each ear, the "pressure" of the first tone had to be increased in the ratio of $1:10^2$ to $1:10^3$ before masking occurred. From this they infer, without sufficient justification in my opinion, that the masking is peripheral, that it is "caused by the conduction of the masking tone through the head" by bone-conduction. They also report "that people very deaf in one ear have been noted for which 10^2 or 10^3 times the current is required for audition with the receiver on the deaf ear over that for the receiver on the good ear"; and that "when the sound for the receiver on the deaf ear is audible, it may be greatly enhanced by placing the finger in the good ear, indicating that the sound is not only heard first in the good ear, but that it arrives there by bone-conduction." It may be that, as Wegel and Lane suggest, there is transmission of sound of this order of magnitude through the head from one ear to the other and that the masking is in some way due to this transmission; but that the masking *is* due to the transmission is pure assumption, and Minton[†] very properly objects to such assumptions being made in the present state of our knowledge. The further inference, that there is *bone-conduction*, is altogether unwarranted. Assuming the transmission there is nothing, in these experiments, to show that it is due to bone-conduction rather than to other possible means of transmission.

42. In this connexion an interesting little experiment was described by Thompson in 1878[‡]. Thompson states that if a small vibrating tuning-fork

> "be pressed against the parietal or occipital regions of the head on the right of the median line, its sound appears to be heard in the left ear. . . . If, however, the fork be pressed against the region immediately above either temporal bone, its sound is heard in the ear of the same side."

---

[*] Wegel and Lane define the magnitude of a tone as "the ratio of its pressure of that of its minimum audible value."

[†] Phys. Rev. xxii. pp. 506–509 (1923).

[‡] Phil. Mag. [5] vi. p. 390 (1878).

43. I have tried this experiment with forks of frequencies 50, 256, 435, 800, and 1000 d.v./sec. I find it very difficult to judge the position of the sound heard when the fork is pressed against the region immediately above either temporal bone; but if any of the above forks, sounding so faintly as to be inaudible when held over the head in the sound-proof room, is pressed on the lateral bones immediately above the right ear, (the fork being so held that the vibrations of the prongs are at right angles to the line joining the ears and the whole of the fork being on the right of the sagittal plane so that the right ear has any advantage which may accrue from the aerial sound-waves leading in phase), the sound is immediately heard and is located on the *left*, i.e., on the further side. If the fork is pressed against the mastoid process behind the right ear, the tone is located on the right. Thompson simply notes the experimental fact, without giving any explanation; and I am equally at a loss for an explanation in conformity with the generally accepted physiological assumption that a sensation can be aroused by the appropriate stimulus only if it acts on the end organ.

V. SUMMARY.

44. This preliminary survey shows that little or no reliable experimental evidence has so far been obtained to support the hypothesis that aerial borne sound-waves of normal intensity, which reach one ear through the auditory meatus, are transmitted through the head to the other ear. I hope to attack the problem in the near future and, with the assistance of the recently perfected means of amplifying electrical currents, it may perhaps be possible to obtain positive results.

45. Till transmission has been proved, it is rather previous to consider how the vibrations are initiated and whether transmission takes place through the bones, the sinuses, the soft parts of the head, or through any combination of these.

XII. *Minimization of Magnetic Leakage and of its Effect in the Magnetic Testing of Bars and Rods.* *By* EDWARD HUGHES, *B.Sc., Ph.D., A.M.I.E.E.*[*]

ABSTRACT.

A MODIFIED form of the Iliovici permeameter is described in which the balance of magnetic potential is determined by a movable yoke. Experimental results are given showing that the magnetic leakage in the specimen under test varies considerably with the flux density and is dependent upon the disposition of the magnetizing coils. Tests performed on mild-steel and cobalt-chrome specimens indicate that the leakage is greatly affected by the permeability of the sample. The influence of the width of the search-coil upon the accuracy of magnetic testing is discussed mathematically. It is shown that a very large error in the determination of the magnetizing force for a given flux density may be involved if the search-coil is narrow; whereas, with a search-coil extending over the length of bar under test, the error is reduced to a small value. Curves are given showing the percentage errors involved with the extended search-coil for different leakages and different flux densities, the flux density being expressed as a fraction of the saturation density.

IN the double bar and yoke method of magnetic testing it is impossible to eliminate magnetic leakage, though it may be reduced by the addition of compensating coils as in the Burrows permeameter. The latter, however, presupposes the four joints to be of equal reluctance—a condition that is often difficult to fulfil. Burrows[†] has pointed out that, with two soft-iron bars tested by the double-bar method, the magnetic leakage between the centres of the bar and of the yoke may amount to 5 per cent.; and it is surprising that so little attention appears to have been devoted to the influence of magnetic leakage upon the accuracy of magnetic testing and to the dependence of the error upon the length of the search-coil.

The tests to be described were performed on bars of mild steel and of cobalt-chrome steel by means of a modified form (fig. 1) of the permeameter described in the 'Proceedings' of the Physical Society of London'[‡]. The apparatus is shown diagrammatically in fig. 2, where *TT* represents the bar to be tested and *A* is a magnetizing coil situated between the two prongs of a movable yoke *Y*. Another magnetizing

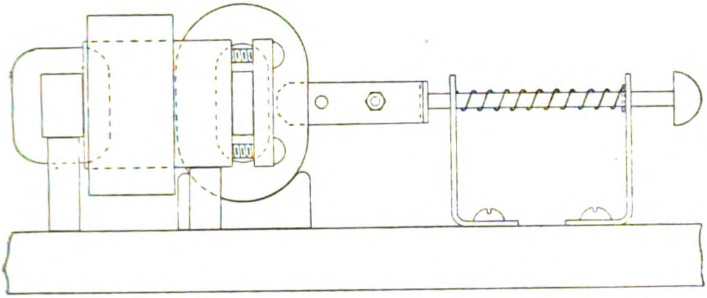
---

[*] Communicated by the Author.

[†] "Determination of Magnetic Induction in Straight Bars," Bull. Bureau of Standards, vi. p. 31.

[‡] "A Magnetic Bridge for testing Straight Specimens," Physical Soc. Proc. xxxvii. p. 233.

Fig. 1.



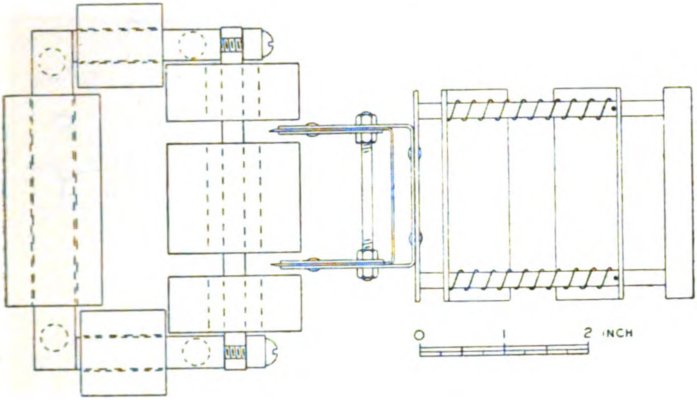
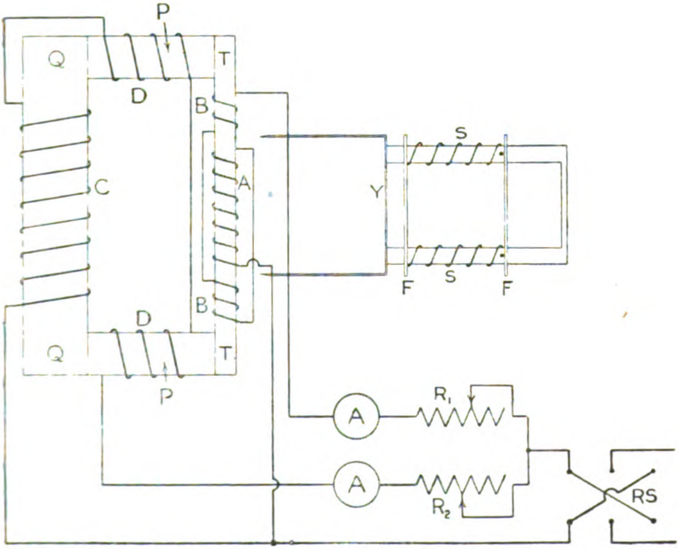


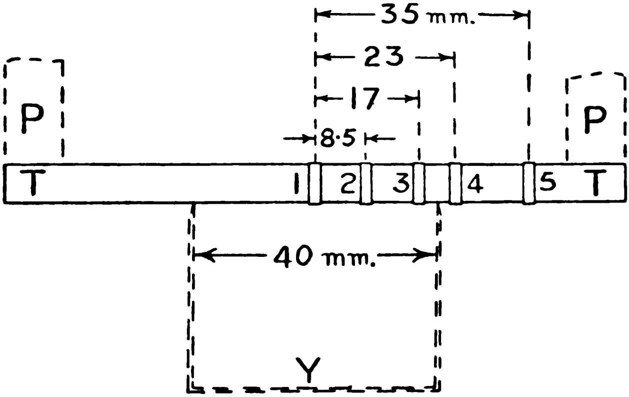
Fig. 2.



M 2

coil *BB* is wound in two sections, one on each side of *A* with sufficient clearance to allow of *Y* being moved backwards and forwards. The magnetic circuit of *TT* is completed through iron yokes *PP* and an iron core *QQ* having windings *DD* and *C* respectively. The coils are connected so that their m.m.f.'s are all acting in the same direction. Five search-coils, each of ten turns, 36 S.W.G., were wound on *TT* in positions indicated in fig. 3. The movable yoke *Y* consists of a strip of Stalloy, 0·5 mm. thick, held by brass plates (fig. 1) which are carried by two rods passing through guide plates *FF* with light springs *SS* to draw *Y* away from *TT*.

Fig. 3.



The operation of the apparatus is as follows:—With a given current through coils *A* and *B*, the current through *C* and *D* is adjusted until no deflexion is obtained on a galvanometer connected to search-coil 1 when the auxiliary yoke *Y* is moved up to *TT*. When a balance has been thus obtained, the points of contact of *Y* with *TT* are at the same magnetic potential, and the m.m.f. of coil *A* is absorbed in sending the flux through that portion of *TT* that lies between these points of contact.

The leakage flux is then measured by reversing the magnetizing currents and noting the deflexions with coils 2, 3, 4, and 5 respectively connected in opposition to coil 1. This leakage flux has been expressed as a percentage of the flux through coil 1; and the results for the mild-steel bar are given in fig. 4. The above test was repeated with different magnetizing currents. It will be observed that both the magnitude and the distribution of the leakage flux vary with different currents and are dependent upon the permeabilities of the specimen and of the yoke.

Fig. 4.

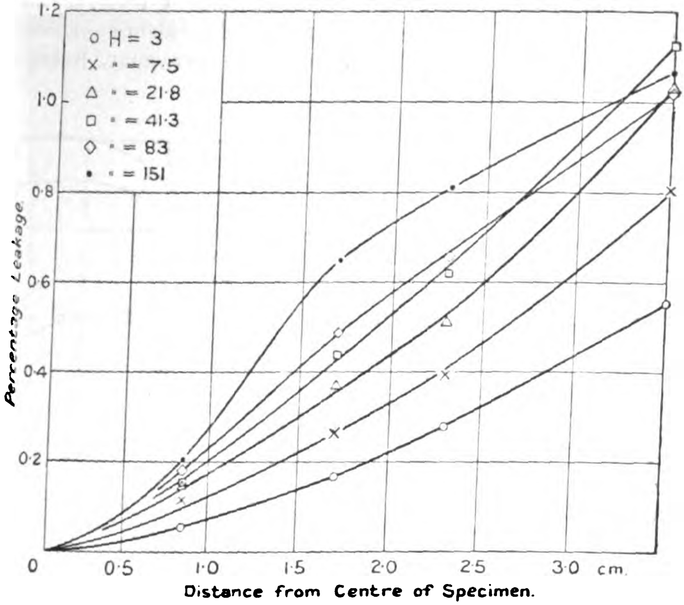


Fig. 5.

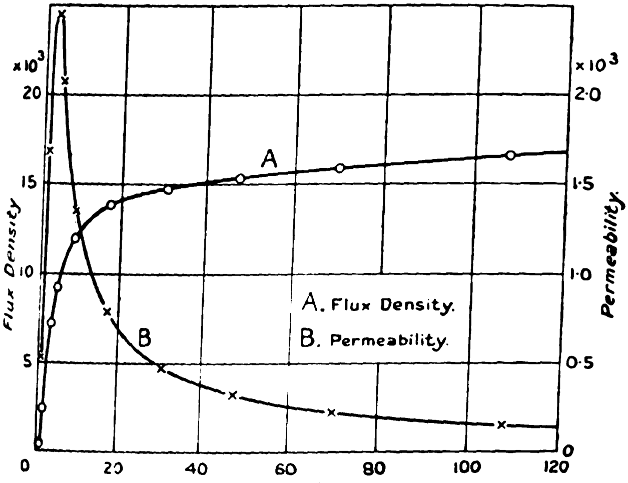
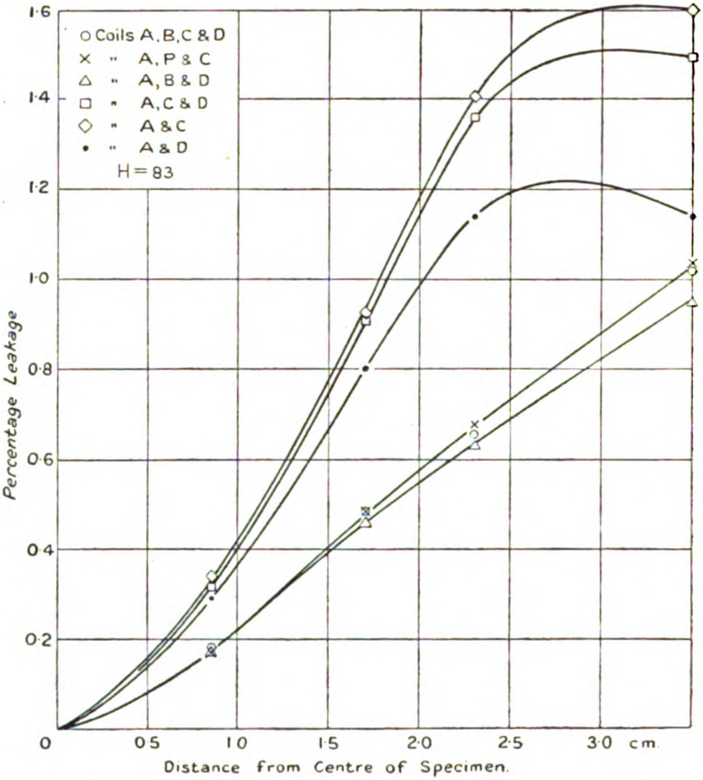


Fig. 5 has been included to show how the flux density and the permeability of this mild steel bar varied with the magnetizing force.

The influence of coils *B*, *C*, and *D* upon the leakage was next investigated. The current through *A* (and through *B* when the latter was in circuit) was kept constant at a value corresponding to H=83, and that through *C* or *D*, or both, was varied until search-coil 1 indicated a balance as already described. The curves in fig. 6 show the percentage leakages with different combinations of coils, and indicate clearly that the leakage is practically the same whether both *C* and *D* or only one of them be in circuit—in other words, that only one of these coils need be employed. The curves also indicate the important contribution of coil *B* towards the reduction of the magnetic leakage—particularly in that portion of the bar that lies inside coil *A*.

Fig. 6.



Similar tests were carried out on a bar of cobalt-chrome steel, the latter being chosen owing to its low permeability.

The results are plotted in figs. 7 and 8, and fig. 9 shows the variation of B and μ with H for this particular specimen. These figures confirm the conclusions derived from the tests on mild steel, and at the same time emphasize the influence of permeability on the magnetic leakage. It will now be obvious that in order to minimize the magnetic leakage in this type of magnetic tester, it is necessary to wind the magnetizing coil over as great a length as possible of the specimen. Windings placed on the yokes, however, contribute practically nothing towards the reduction of leakage.

Fig. 7.

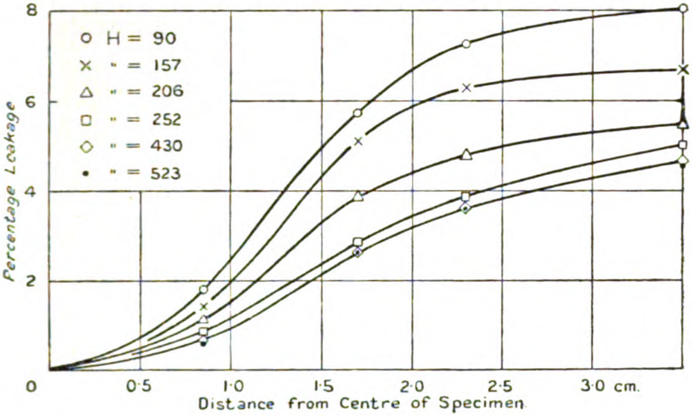
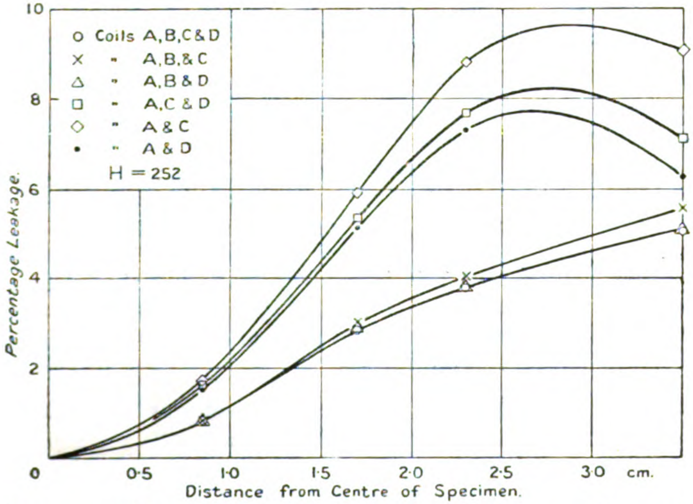
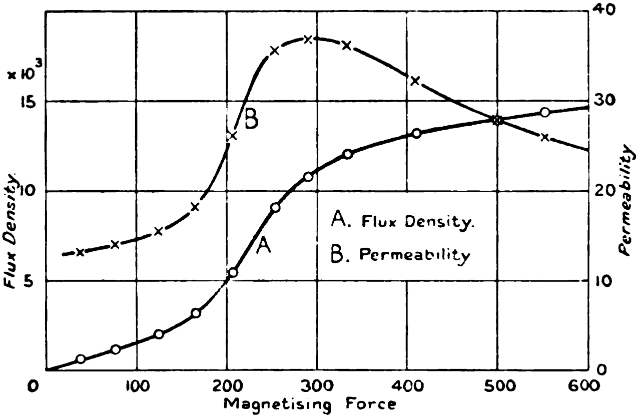


Fig. 8.



It is now essential to consider the extent to which the width of the search-coil affects the error introduced by the existence of magnetic leakage. If the coil be narrow and wound midway along the specimen, it will obviously be measuring the maximum flux density, whereas the magnetizing force calculated from the ampere-turns on the coil is less than that corresponding to the maximum flux density.

Fig. 9.



On the other hand, if the search-coil is wound over the length of bar under test, the mean flux density is obtained. Neither of these alternatives is quite correct; and we shall now proceed to compare their results with that obtained by integrating the magnetizing force over the length under test.

From figs. 4 and 7 it is evident that over the distance spanned by the prongs of *Y* (fig. 3) the leakage curves are intermediate between linear and parabolic curves. We shall therefore consider two cases:—

(*a*) When the leakage flux varies directly as the distance from the centre of the specimen.

(*b*) When the leakage flux varies as the square of the distance from the centre of the specimen.

Case (*a*).

Let $2l$ be the length of bar under test, *i. e.* the distance between the prongs of yoke *Y* (fig. 2). Let B_m be the maximum flux density and B_x the flux density at distance x

from the centre (fig. 10). Let s be the magnetic leakage—expressed as a fraction of B_m—at distance l from centre. Then

$$B_x = B_m(1-sx/l).$$

If T be the number of turns on a search-coil occupying length $2l$,

$$\text{flux linkages over length } dx = B_m(1-sx/l)\frac{T\,dx}{2l},$$

$$\therefore \quad \text{total flux linkages} = 2\int_0^l \frac{B_m T}{2l}\left(1-\frac{sx}{l}\right)dx$$

$$= B_m T(1-s/2).$$

If B_{av} be the average flux density,

$$B_{av} = B_m(1-s/2).$$

If H_{av} be the magnetizing force corresponding to B_{av},

$$\text{Reluctivity} = \frac{H_{av}}{B_{av}} \doteqdot a + \frac{H_{av}}{B_s} = a + bH_{av}\,^{*},$$

where B_s = saturation density = (say) $1/b$,

and a = a constant for a given specimen.

Also, $bB_m = B_m/B_s$; so that the term bB_m, which occurs frequently in the following calculations, represents *the ratio of the flux density at the centre of the bar to the saturation density of the material.*

Substituting for B_{av} in the above expression, we have

$$H_{av} = \frac{aB_m(1-s/2)}{1-bB_m(1-s/2)},$$

and total m.m.f. $= 2H_{av}l$

$$= \frac{2laB_m(1-s/2)}{1-bB_m(1-s/2)}. \quad . \quad . \quad . \quad . \quad (1)$$

Hence we can calculate in terms of B_m the m.m.f. that would be required if the flux density were uniform along the specimen at the mean values given by a search-coil of length $2l$. Thus, if s be 0·05 and B_m be 0·8 of the saturation density,

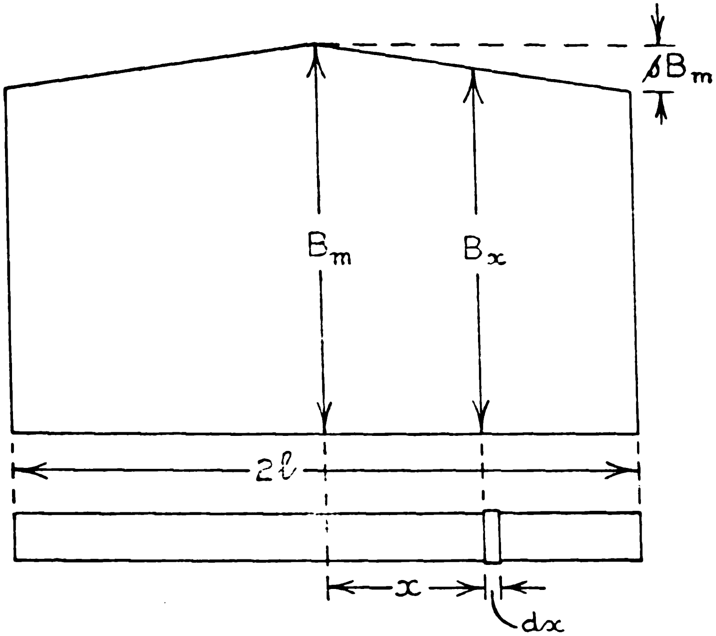
$$\text{total m.m.f.} = 8{\cdot}865\,laB_m. \quad . \quad . \quad . \quad . \quad (2)$$

---

[*] For simplicity, the actual flux density is used instead of the ferromagnetic density.

Let us now calculate the actual m.m.f. required when the flux is distributed as shown in fig. 10.

Fig. 10.



If H_x be the magnetizing force corresponding to flux density B_x in the above figure, then

$$\frac{H_x}{B_x} = a + bH_x.$$

Substituting for B_x in terms of B_m, we have

$$H_x = \frac{aB_m}{1-bB_m} \times \frac{1-\frac{sx}{l}}{1+\frac{bB_m sx}{l(1-bB_m)}},$$

$$\therefore \text{ total m.m.f.} = 2\int_0^l H_x dx$$

$$= \frac{2al}{b^2 sB_m} \log\left(1+\frac{bB_m s}{1-bB_m}\right) - \frac{2al}{b}$$

$$= \frac{alB_m}{1-bB_m}\left\{2 - \frac{s}{1-bB_m} + \frac{2}{3}\cdot\frac{s^2 bB_m}{(1-bB_m)^2} - \frac{2}{4}\cdot\frac{s^3 b^2 B_m^2}{(1-bB_m)^3} + \dots\right\}. \quad (3)$$

Taking the values of $s=0{\cdot}05$ and $bB_m=0{\cdot}8$ assumed on p. 169, and substituting in the above expression, the terms being continued until negligibly small, we have

$$\text{total m.m.f.} = 8{\cdot}895alB_m. \quad . \quad . \quad . \quad . \qquad (4)$$

Comparison of (2) and (4) shows that for these particular values of the leakage and of the flux density, the m.m.f. corresponding to the mean flux density is 0·34 per cent. less than the m.m.f. calculated for a linear variation of the flux density.

Values of the m.m.f. have been calculated from expressions (1) and (3) for different values of leakage and of flux density; and the difference between the corresponding values has been expressed as a percentage of the m.m.f. calculated from (3). For instance, with

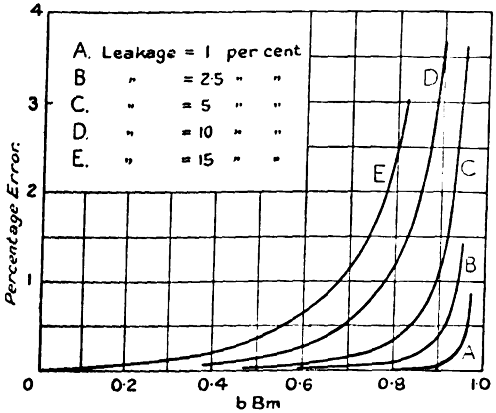
$$s = 0{\cdot}05 \text{ and } bB_m = 0{\cdot}8,$$

$$(\text{m.m.f.})_1 = 8{\cdot}865alB_m,$$

$$\text{and} \quad (\text{m.m.f.})_3 = 8{\cdot}895alB_m.$$

The difference between the two expressed as a percentage of $(\text{m.m.f.})_3$ is 0·34. These results have been plotted in fig. 11,

Fig. 11.



from which it follows that with flux densities less than 90 per cent. of the saturation value, the error involved in the determination of the m.m.f.—even for a leakage of 5 per cent.—can be limited to 1 per cent. by merely winding the search-coil over the length of specimen under test.

It may be added that in magnetic testing the flux density is seldom taken up to 90 per cent. of the saturation value. Also, at high flux densities, the expression given above for the magnetic reluctivity is only approximate, since it neglects H in comparison with B; whilst heterogeneity of the material causes the slope* of the reluctivity curve to decrease.

Had the search-coil been narrow and wound halfway along the specimen, the maximum flux density B_m would have been measured. If H_m be the true magnetizing force for this flux density, then

$$\frac{H_m}{B_m} = a + bH_m,$$

$$\therefore \quad H_m = \frac{aB_m}{1-bB_m},$$

$$\text{and total m.m.f. for a length } 2l = \frac{2laB_m}{1-bB_m}$$

$$= 10laB_m \quad \text{for} \quad bB_m = 0{\cdot}8,$$

a value that is 12·4 per cent. greater than the m.m.f. as calculated from the distribution of flux by expression (3). This is sufficient to show the enormous error that may be introduced by the use of a narrow search-coil.

Case (*b*).

The leakage flux is assumed to vary as the square of the distance from the centre of the specimen. Using the same symbols as before, we have from fig. 12,

$$B_x = B_m - \left(\frac{x}{l}\right)^2 sB_m,$$

$$\therefore \text{ total flux linkages} = 2\int_0^l \frac{B_m T}{2l}\{1-(x/l)^2 s\}dx$$

$$= B_m T(1-s/3).$$

If B_{av} be the average flux density,

$$B_{av} = B_m(1-s/3).$$

---

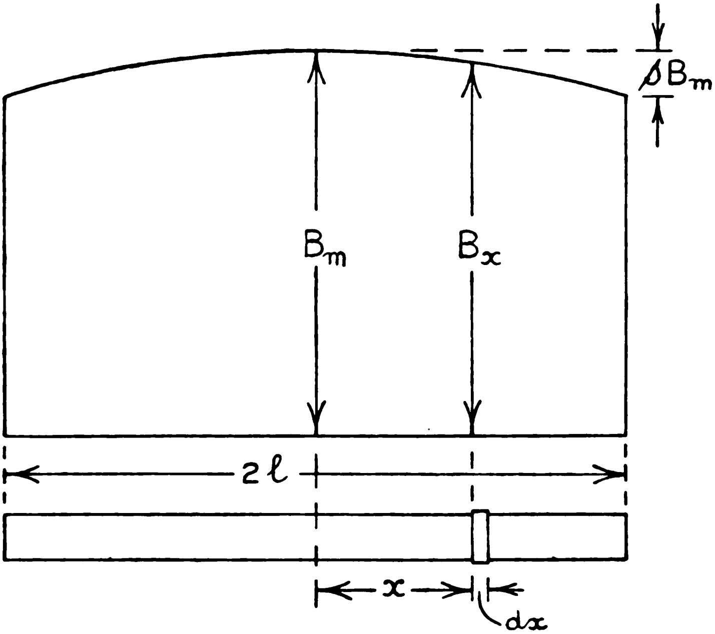
* Physical Soc. Proc. xxxvii. p. 238.

But
$$\frac{H_{av}}{B_{av}} = a + bH_{av},$$
$$\therefore \quad H_{av} = \frac{aB_m(1-s/3)}{1-bB_m(1-s/3)},$$

and total m.m.f. $= 2lH_{av}$

$$= \frac{2laB_m(1-s/3)}{1-bB_m(1-s/3)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Fig. 12.



For example, if s be 0·05 and bB_m be 0·8, as on p. 169,

$$\text{total m.m.f.} = 9{\cdot}2166laB_m. \quad . \quad . \quad . \quad . \quad (6)$$

Let us now calculate the actual m.m.f. for the assumed flux distribution (fig. 12),

$$\frac{H_x}{B_x} = a + bH_x.$$

Substituting for B_x, we have

$$H_x = \frac{aB_m\left(1-\frac{sx^2}{l^2}\right)}{(1-bB_m)\left\{1-\frac{bB_m sx^2}{l^2(1-bB_m)}\right\}},$$

$$\therefore \text{ total m.m.f.} = 2\int_0^l H_x dx$$

$$= \frac{2aB_m}{1-bB_m}\left\{-\frac{l(1-bB_m)}{bB_m} + \frac{l}{bB_m}\sqrt{\frac{1-bB_m}{bB_m s}} \,.\, \tan^{-1}\sqrt{\frac{bB_m s}{1-bB_m}}\right\}$$

$$= \frac{2alB_m}{1-bB_m+bB_m s}\left[(1-s) + \frac{s}{1-bB_m+bB_m s}\left\{\frac{2}{3}+\frac{2\,.\,4}{3\,.\,5}\left(\frac{bB_m s}{1-bB_m+bB_m s}\right) + \frac{2\,.\,4\,.\,6}{3\,.\,5\,.\,7}\left(\frac{bB_m s}{1-bB_m+bB_m s}\right)^2 + \ldots\right\}\right]. \quad (7)$$

Taking $s=0{\cdot}05$ and $bB_m=0{\cdot}8$, as above, and substituting in expression (7)—the terms being continued until negligibly small—we have

$$\text{total m.m.f.} = 9{\cdot}2526laB_m. \quad . \quad . \quad . \quad . \quad (8)$$

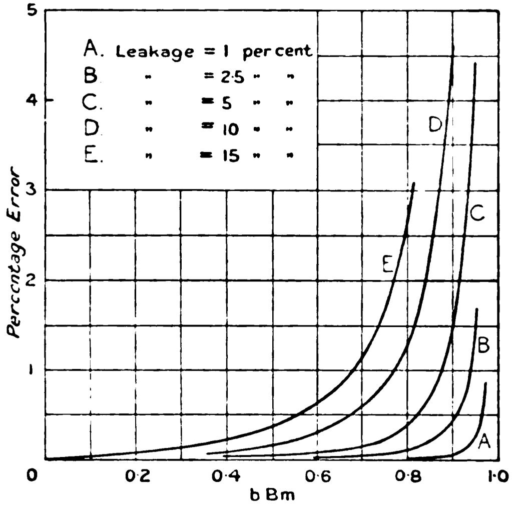
Comparison of (6) and (8) shows that, at the above values of leakage and of flux density, the m.m.f. corresponding to the mean flux density is 0·39 per cent. less than that calculated for a parabolic variation of the leakage flux.

The difference between the m.m.f.'s derived from expressions (5) and (7) has been calculated as a percentage of the latter m.m.f. for different values of s and bB_m, and the results are given in fig. 13.

Since the curves of actual leakage flux (figs. 4 and 7) are intermediate between those assumed for deriving figs. 11 and 13, it is evident from these figures that, by winding the search-coil over the length of bar under test, the error involved in the measurement of m.m.f. is less than 1 per cent., except at very high values of the flux density and of the magnetic leakage.

It may be added that, with parabolic variation of leakage flux and the above value of bB_m, the m.m.f. corresponding to B_m—namely, the flux density measured with a narrow search-coil—is 8·1 per cent. greater than the actual m.m.f. given by expression (8).

Fig. 13.



Conclusions.

(1) With the double bar and yoke method of magnetic testing arranged so that two symmetrical points on the specimen under test may be adjusted to be at the same magnetic potential, the flux density is a maximum midway along the specimen; and the magnetic leakage increases more rapidly than the distance from the centre, but less rapidly than the square of that distance.

(2) The magnitude and the variation of the magnetic leakage depend upon the permeabilities of the bar and of the yoke.

(3) With this type of tester, the distribution of the flux along the specimen is practically independent of the distribution of the magnetizing coil on the second bar and on the yoke, but is greatly affected by the length of the magnetizing coil on the specimen.

(4) With the apparatus shown in fig. 1, the magnetic leakage over the length for which the m.m.f. is determined has an average value of about 0·5 per cent. for mild steel when tested over a wide range of magnetizing force. For

cobalt-chrome steel, the corresponding value is about 4 per cent.

(5) By winding the search-coil over the length under test, the error due to magnetic leakage can be reduced to an extremely small value — even with comparatively large leakage; and, since magnetic leakage cannot be entirely eliminated in bar tests, the search-coil should always extend over the length for which the m.m.f. is being determined.

(6) Above a certain percentage of the saturation density—depending upon the percentage leakage—the error due to magnetic leakage increases rapidly; but such values of flux density require very high magnetizing forces and are seldom attained in magnetic testing.

The author desires to express his thanks to the Principal and the Governors of the Municipal Technical College, Brighton, for facilities to carry out the experimental work described in this paper.

XIII. *The Effect of a Magnetic Field on the Electrical Resistance of Mercury and some Amalgams.* *By* PHYLLIS JONES, *B.Sc.*, *and* T. J. JONES, *M.Sc.* (*Research Students, University College of Swansea*)*.

INTRODUCTION.

THE effect of a transverse magnetic field on the electrical resistance of mercury has been examined by Drude and Nernst †, Berndt ‡, Rossi §, and Nielson ||. All the above observers obtained small increases of resistance due to the magnetic field, but Berndt noticed that the increase of resistance was less, the smaller the diameter of the tube. He found that for a field of three kilogauss, and a column of 0·29 mm. diameter, the change of resistance was less than 0·00005 per cent. Rossi investigated the change of resistance in mercury and in bismuth amalgams, and found that the change of resistance increased with the field, the diameter of the column, and the concentration of the amalgam.

Berndt came to the conclusion that if there were true magneto-resistance effects in mercury, they must be small

---

* Communicated by Prof. E. J. Evans, D.Sc., University College of Swansea.

† Drude and Nernst, *Wied. Ann.* xlii (1891).

‡ G Berndt, *Ann. d. Phys.* xxiii. (1907).

§ R. Rossi, *Nuov. Gim.* (6), ii. (1911).

|| Nielson, Phys. Rev. p. 302, Feb. 1924.

compared with those obtained in the case of solid metals. This conclusion is confirmed by the work of Nielson, who used very fine tubes, and found an increase of resistance of 0·0003 per cent. for a magnetic field of sixteen kilogauss.

Recently two papers dealing with the problem have been published: one, mainly theoretical, by Williams [*], and the other, containing the results of experimental work, by Jones [†].

Williams, in his paper, assumes that the change of resistance of a column of mercury under the action of a transverse magnetic field is due to the two following causes:—

(i.) A change of resistance analogous to that observed in a solid metal (*i. e.* a true effect).

(ii.) A change of resistance, due to the development by the mechanical action of the magnetic field on the current, of mass motion of the mercury.

The first effect is proportional to the resistance r in the field, and the change of resistance due to this effect alone may, for a given field, be expressed by $\delta r_1 = Ar$, A being a constant for that field. The experiments carried out by Nielson show that for a field as large as sixteen kilogauss, A cannot be greater than 3×10^{-6}.

In the theoretical consideration of the second effect the motion of the mercury is regarded as being completely determined by the mechanical force "hi" (where "h" is the intensity of the magnetic field and "i" the current), the viscosity η, the density ρ, and the scale s, which is a measure of the various lengths involved in the system.

Dimensional analysis then gives for the change of resistance δr_2 arising from the motion of the mercury the general relation

$$\delta r_2 = \mathrm{B}\frac{h^2 s}{\eta} f\left(\frac{\eta^2}{his\rho}\right)\phi\left(\frac{\sigma}{\sigma'}\right), \quad . \quad . \quad . \quad . \quad (1)$$

where f and ϕ are any functions, B a numerical constant, and σ/σ' the ratio of the resistivity of the leads to that of the mercury. If the leads are sufficiently far removed from the field, the term $\phi\ (\sigma/\sigma')$ is a constant which can be included in B, and hence the total increase of resistance is

$$\delta \mathrm{R} = \delta r_1 + \delta r_2 = \mathrm{A}r + \mathrm{B}\frac{h^2 s}{\eta} f\left(\frac{\eta^2}{his\rho}\right). \quad . \quad . \quad (2)$$

---

[*] E. J. Williams, Phil. Mag. July 1925, pp. 27–46.

[†] T. J. Jones, Phil. Mag. July 1925, pp. 46–60.

It has been shown that if the motion of the mercury is steady, equation (2) reduces to

$$\delta \mathrm{R} = \mathrm{A}r + \mathrm{B}\frac{h^2 s}{\eta}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

However, if the motion of the mercury is turbulent, the change of resistance depends on the magnitude of the current, and is given by

$$\delta \mathrm{R} = \mathrm{A}r + \mathrm{B}\frac{h^{1+y} s^y}{i^{1-y}\eta^{2y-1}\rho^{1-y}}. \quad . \quad . \quad . \quad (4)$$

This formula can be simplified in the case of straight cylindrical tubes of diameter d, and assumes the form

$$\delta \mathrm{R} = \mathrm{A}r + \mathrm{B}\frac{h^{1+y} d^{y+\beta}}{i^{1+y}\eta^{2y-1}\rho^{1-y} t^{\beta}}, \quad . \quad . \quad . \quad (5)$$

where t represents the distance apart of the pole pieces and y and β are constants.

Jones * showed from his experiments that the comparatively large increase of resistance obtained in his experiments could be regarded as being altogether due to the turbulent motion set up in the mercury by the magnetic field, and that the value of y in equations (4) and (5) is 0·59. He also found for straight cylindrical columns that equation (5) could be written as

$$\delta \mathrm{R} = \mathrm{B}\frac{h^{1\cdot59} d}{i^{\cdot41}\eta^{\cdot18}\rho^{\cdot41} t^{\cdot41}}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

His experiments were carried out with straight tubes of diameters of about 0·5 cm. carrying currents varying from 0·5 to 5 amperes, and placed in a transverse magnetic field of two to ten kilogauss.

The present investigation was carried out to study the effects in tubes of smaller diameter and carrying smaller currents. It was hoped in this way to obtain the conditions necessary for steady motion, in order to verify, if possible, equation (3), in the case when the change of resistance is entirely due to motion,

$$i.e. \qquad \delta \mathrm{R} = \delta r_2 = \mathrm{B}\frac{h^2 s}{\eta}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In this case the resistance should vary as the square of the field and inversely as the viscosity of the mercury.

---

* *Loc. cit.*

In this connexion Williams[*] examined the results obtained for mercury by Rossi, who used tubes of diameters 0·7 and 0·5 mm. and fields varying from 3350 to 4450 gauss. Williams showed that $\frac{\delta R}{h^2}$ was approximately constant; but since the current passing through the mercury column was not recorded, and also the variation in the magnitude of the field was small, the experiments were not satisfactory as a test of the theory.

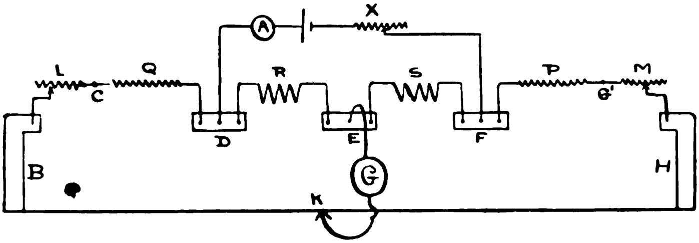
Rossi, as already stated, investigated the effect of a magnetic field on the resistance of bismuth amalgams, and found that the change of resistance increased as the concentration of the amalgam varied from 0·5 per cent. of bismuth to an amalgam saturated with the metal at 12° C. Williams, in his paper[†], analyses Rossi's results, and on certain assumptions concludes that, in order to account for the experimental results, it is necessary to assume the existence of a true resistance change in bismuth amalgams.

It was therefore considered of some importance to examine the effect of a transverse magnetic field on the resistance of amalgams, and for this purpose amalgams containing 0·5 per cent. of bismuth and 1·187 per cent. of zinc were investigated.

Experimental Arrangement.

The Wheatstone bridge method was used to determine the changes of resistance produced by the magnetic field, and the connexions are shown in fig. 1.

Fig. 1.



R is the column of mercury which is placed in the magnetic field and is connected to the bridge by means of long flexible leads. S is a comparison column of mercury of nearly the same dimensions and resistance as R, and is connected to the bridge by flexible leads running close to those joining R to the bridge. The resistance S is out of the influence of the field, and the copper leads immersed in the mercury are for each tube out of the magnetic field. The resistances R and S, when the mercury was contained in bent tubes, were both immersed in a copper bath containing water, but when the columns were straight, variations of temperature were avoided as far as possible by surrounding the tubes with cotton-wool. The resistances P and Q between F and G′ and C and D respectively were 10-ohm manganin resistance coils, and were placed together in the same enclosure. M and L are also manganin resistance coils which could be varied in order to maintain a balance on the bridge wire joining B and H. The bridge wire was made of manganin, and had a resistance of 10^{-4} ohm per cm. The source of E.M.F. was a battery consisting of one or two storage cells and the current passing into the bridge system could be varied by means of a resistance X, and was measured by a Weston ammeter (A).

---

[*] *Loc. cit.* p. 35.

[†] *Loc. cit.* pp. 36–38.

A sensitive Moll galvanometer (G) was employed to determine the change of resistance due to the magnetic field. Its zero was found to be very constant, and a microvolt applied to its terminals produced a deflexion of 6·46 mm. when the scale was at a distance of 162 cm. It had a period of about 1·5 seconds, and this quickness of action was found very useful in experiments of this type, where the conditions are continually changing and the increases of resistance to be measured are comparatively small.

The magnetic fields were obtained by means of a large circular electromagnet having pole-pieces 8 cm. in diameter at a distance apart of 1·65 cm. The fields used in the present experiments varied from 3000 gauss to 10,000 gauss, and were measured with a Grassot fluxmeter. The magnetic fields corresponding to known magnetizing currents were measured from time to time and found to be constant.

Two types of glass tubes, as shown in figs. 2 and 3, were used in the present experiments. In some cases it was only necessary to keep the tube in position, and investigate the effect of varying one of the quantities involved, such as the intensity of the field, on the increase of resistance. In other cases it was necessary to remove the tube and replace it in exactly the same position.

The magnitude of the effect depends upon the position of the tube with respect to the magnetic field, and consequently the method of mounting the tubes was so designed as to

Fig. 2.

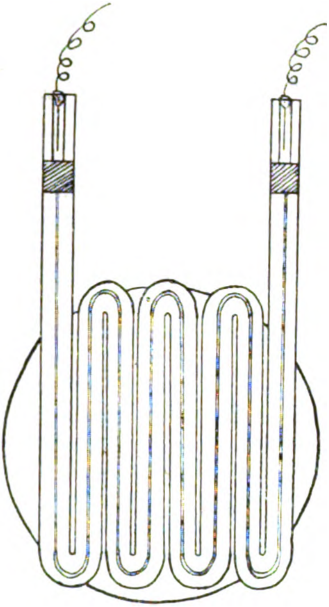
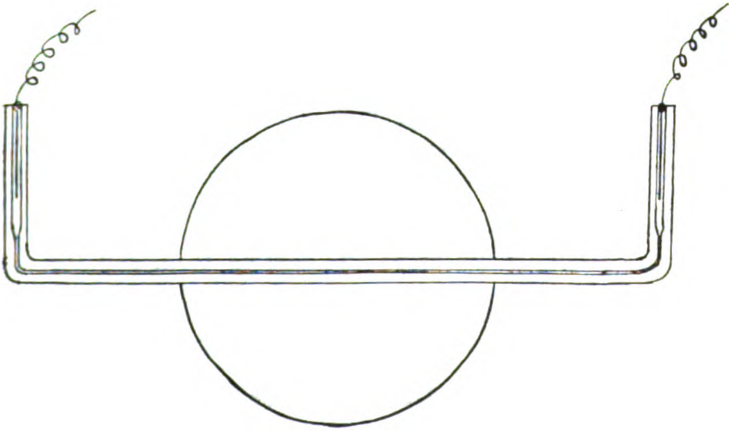


Fig. 3.



make it possible to replace the tube in exactly the same position when necessary. The changes of resistance were determined as follows :—

The bridge was first balanced when the magnet was not excited, and the position of the fine line in the image of the spot of light on the scale was noted. The magnetizing circuit was then closed and the new position of the spot of light noted. Finally, the magnet circuit was broken and zero position again noted. The difference between the mean of the first and third readings and the second was taken as the deflexion produced by the magnetic field. Sometimes the mode of procedure was varied, and the bridge was first balanced with the magnetic field on, and the deflexion produced on breaking the magnetic circuit measured in a similar manner.

The deflexions measured in this investigation varied from about 2 mm. to about 12 cm., depending upon the intensity of the magnetic field and the magnitude of the current passing through the mercury column. The definition of the light-spot was so good that the position of the line could be estimated to 1/10th of a mm. When the current passing through the mercury was small, and the temperature of the column approximately that of the room, the difference between the two zero readings (the first and third mentioned above) was small, and in a large number of cases the two readings were identical. When, however, the currents sent through the mercury were of the order of 1 ampere, the Joule heating-effects and, to a smaller extent, the heat produced by the magnet caused trouble, and the difference between the two zeros was appreciable. It was found possible to take satisfactory readings in this case, and only observations in which the difference between the first and third readings was small in comparison with the total deflexion, were finally considered.

When investigating the effect of temperature (or viscosity) on the change of resistance, the spot of light was found to be a little unsteady and the values of the deflexions were not as constant as in the experiments carried out at room temperatures. In these experiments the outside limbs of the bent tube were out of the heating bath, and the unsteadiness was probably caused by thermoelectric currents, due to slight temperature differences in the two mercury tubes. The effect was diminished by wrapping the limbs with asbestos cord.

From the magnitudes of the deflexions, knowing the sensitivity of the galvanometer and the magnitude of the current entering the bridge whose resistances were also known, it is possible from the well-known Wheatstone bridge equations to calculate the change of resistance produced in the mercury by the magnetic field. Since the change of resistance in these experiments is small, and of the order of 10^{-5} ohm, the deflexion due to it is proportional to the product of the change of resistance and the current passing through the mercury resistance in the field.

When the deflexions are about 1 cm. or more, and the experiments are carried out in tubes of diameter 1·1 mm. under ordinary circumstances at room temperature and using currents between ·03 and ·5 amp., it is considered that the results are correct to within 3 or 4 per cent. The results obtained with narrow tubes of diameter about 0·5 mm. are not as accurate, and only small currents were used, owing to the heating effect of the current and the difficulties caused by air-bubbles. The variation of temperature during the course of a set of experiments was not greater than about 5° C., and during the whole period of experimenting the temperature only varied from about 9° C. to about 17° C. The changes in the value of δR, due to a change of temperature of this amount, are within the experimental error involved in the determination of δR.

In this investigation, as was also shown previously by Jones [*], the increase of resistance observed is not related to the magnitude of the resistance in the field. The effect is probably produced by motion set up in the mercury at points in the tube, where either the magnetic intensity or the current density changes in value, and consequently a change in the position of the tube (especially the bent tube) will cause an appreciable change in the value of δR.

In the present experiments the resistance in the field was about 87 per cent. of the total resistance of the mercury column for the bent tube, and varied from about 30 per cent. to 40 per cent. in the case of straight tubes.

EXPERIMENTAL RESULTS.

The Variation of δR *for mercury with the current "i" and the magnetic field "h."*

Experiments were carried out with bent tubes of diameters 1·1 mm. and 0·4 mm. and with a straight tube of diameter

---

[*] *Loc. cit.*

0·96 mm. In the case of the bent tube of 0·4 mm. diameter, experiments were carried out for small currents only, as the Joule heating effect made accurate observations impossible for currents of the order of 0·3 ampere. The experimental results are given in Tables I., II., and III.

TABLE I.

Bent tube of diameter 1·1 mm.
Resistance of mercury column in field = 0·64 ohm.
Total resistance of mercury column = 0·76 ohm.

h in gauss.	$\delta R \times 10^6$ ohms for currents ranging from ·03 to 1·4 amperes.									
	·03	·047	·065	·14	·338	·476	·772	1·144	1·256	1·395
10,000...	56·4	56·52	56·57	54·66	47·69	43·59	37·84	33·9	32·8	31·52
9,000...	45·38	45·93	45·76							
8,150...	37·1									
7,750...	...	...	36·63							
7,071...	...	...	28·29	...	25·78	...	...	...	...	18
6,500...	...	24·12								
6,000...	...	...	20·42							
4,814...	...	...	13·01	...	12·89	...	...	...	...	9·696
4,101...	...	...	9·36							
3,198...	...	...	5·657							

TABLE II.

Bent tube of diameter 0·4 mm.
Resistance of mercury in the field = 4·89 ohms.
Total resistance of mercury column = 5·38 ohms.

h in gauss.	$\delta R \times 10^6$ ohms for currents of ·039 and ·078 ampere.	
	·039	·078
10,000	24·36	22·04
7,071	11·06	11·94

Table III.

Straight tube of diameter 0·96 mm.
Resistance of mercury column in field = ·106 ohm.
Total resistance of mercury column = ·36 ohm.

h in gauss.	$\delta R \times 10^6$ ohms for currents ranging from ·068 to ·58 ampere.					
	·068	·097	·145	·29	·386	·58
10,000......	28·84	27·653	26·228	22·81	20·14	16·93
7,071......	14·62	13·828	13·59	...	11·76	
4,814......	...	6·049	...	...	6·518	

Variation of δR *with the Current* "i."

If the results collected in Table I. (bent tube of diameter 1·1 mm.) are examined, it is evident that for currents of ·03, ·047, ·065 ampere, the value of δR is independent of the current. As the magnitude of the current increases, the value of δR diminishes, and if, for a constant field, $\delta R \propto \frac{1}{i^x}$, the value of the index "x" for two given currents can be determined from the experimental results. If, for instance, the values of δR for currents of ·338 and ·476 ampere and a field of 10,000 gauss are taken, the value of "x" is found to be ·26. The value of "x" calculated from two currents increases as the magnitudes of the currents increase, until it becomes ·37 for currents of 1·144 and 1·395 amperes. Unfortunately, larger currents could not be passed through the tube, owing to experimental difficulties caused by the Joule heating effect.

Similar results are obtained if Table III., which gives the results with a straight tube, is examined.

For currents of ·068 and ·097 ampere the value of δR for a given field is, within experimental error, independent of the current. As the current increases, the value of δR corresponding to a given field (10,000 gauss) diminishes, and the index "x" increases until it reaches an almost constant value. The value of "x" for currents of ·145 and ·29 ampere and a field of 10,000 gauss is ·2, and for currents of ·29, ·386, and ·58 ampere, taken in pairs, assumes an approximately constant value of ·43.

Jones had previously shown for large currents in wide tubes that, for a constant value of the field, $\delta R \propto \frac{1}{i^{\cdot 42}}$, a result in agreement with Williams's theory, if the magnetic field produces turbulent motion in the mercury.

In the present experiments it has been shown that, for narrower tubes and smaller currents, δR is independent of the current. This result is also in agreement with Williams's theory, if the mercury is in steady motion. Furthermore, it is seen that as the current passing through the mercury increases, the value of "*x*" increases from 0 to 0·43, which is practically the same value as obtained by Jones.

The Variation of δR *with "h."*

In order to consider the variation of δR with the field for a constant current, Tables IV. and V. have been constructed from the results collected in Tables I. and III.

TABLE IV.

Bent tube of diameter 1·1 mm.

"*h*" in gauss.	$\frac{\delta R}{h^2} \times 10^{14}$.		$\frac{\delta R}{h^{1\cdot 79}} \times 10^{13}$.	$\frac{\delta R}{h^{1\cdot 61}} \times 10^{12}$.
	·03 amp.	·065 amp.	·338 amp.	1·395 amps.
10,000	56·4	56·57	32·993	11·45
9,000	56·02	56·49		
8,150	55·85			
7,750	...	55·99		
7,071	...	56·58	33·159	11·41
6,000	...	56·72		
4,814	...	56·13	33·009	11·42
4,101	...	55·65		
3,198	...	55·31		

TABLE V.

Straight tube of diameter 0·96 mm.

"h" in gauss.	$\frac{\delta R}{h} \times 10^{14}$.		$\frac{\delta R}{h^{1\cdot54}} \times 10^{12}$.
	·068 amps.	·097 amp.	·386 amp.
10,000	28·84	27·656	13·93
7,071	29·24	27·66	13·87
4,814	...	26·10	13·897

From these tables it follows that, for low values of the current, δR is proportional to h^2 for both the bent and straight tubes. This result is in agreement with Williams's theory when the mercury is in steady motion. As the current increases, $\delta R \propto h^x$, where "x" assumes values smaller than 2. In the case of the bent tube, the smallest value reached by "x" is about 1·61, which is not far removed from the constant value 1·58 obtained by Jones for large currents passing through mercury contained in wider tubes. In the case of the straight tube the smallest value of "x" was 1·54, which, again, is in fairly good agreement with Jones's value.

The experimental results collected in Tables I. and III. show that, for small currents passing through mercury contained in tubes of diameter about 1 mm., $\delta R \propto h^2$, and is independent of the current. As the current increases, δR becomes dependent on the current, until finally $\delta R \propto \frac{h^{1\cdot57}}{i^{\cdot43}}$. The latter result was first obtained by Jones, and both results support the theory put forward by Williams.

The experiments with a narrow tube of diameter 0·4 mm. were carried out to determine the value of $\frac{\delta R}{R}$ for a given value of "h" when a large resistance was placed in the magnetic field. The results of other observers, in the case of mercury, have often been given in this form, but Jones, in the case of wide tubes, had shown that δR does not depend on the resistance in the field.

A comparison of the results obtained with the two tubes for a given field shows that δR is less for the tube of the smaller diameter, although the resistance in the field is 7·6 times greater than for the tube of large diameter. The result supports the view that the increase of resistance is due to motion set up in the mercury. The two tubes were not similar, as the one of smaller diameter had more bends in it than the other. The results cannot, therefore, be employed to study the effect of diameter on the increase of resistance of δR. The results with this tube are not as accurate as those obtained with the tube of larger diameter, as the deflexions measured were small. For instance, the deflexion measured for a current of ·08 ampere for a field of 7071 gauss was only 1·26 mm.

The value of $\frac{\delta R}{R}$ for a field of 10,000 gauss and a current of ·04 ampere is $4{\cdot}1\times10^{-6}$ ohm, and the motion in this case is probably steady.

Variation of δR *with Temperature.*

These experiments were carried out to determine the change in the value of δR with rise of temperature of the mercury. Jones[*] had previously shown that the increase of resistance $\delta R \propto \frac{1}{\eta^{\cdot 18}}$ in the case of wide tubes carrying large currents. A relation of this type is to be expected on Williams's theory, if the motion of the mercury is turbulent. If, however, the motion is steady, the increase of resistance should vary inversely as the viscosity η.

Experiments were, therefore, carried out on mercury contained in a bent tube of diameter 1·1 mm., carrying a current of ·065 ampere and placed in a magnetic field of 10,000 gauss. The change in resistance δR was measured at room temperature, the temperature of boiling water, and the temperature of boiling aniline. In order to get rid of air-bubbles, the tubes containing the mercury were heated to temperatures higher than those used in the present experiments, and the mercury sucked through the tubes in both directions. The deflexions observed were slightly variable, but it is hoped that the mean values are correct to within about 8 per cent. These experiments will again be repeated under more satisfactory conditions.

The value of δR was re-determined at room temperature after heating to a higher temperature, and found to be the same as the initial value within experimental error. The expansion of the glass, due to the rise of temperature, has no appreciable effect on the magnitude of the current passing through the tubes, and the change of diameter of the tube can be neglected when considering the variation of δR with the viscosity η. The bent tube, which was placed in the magnetic field when experiments were carried out at the temperature of boiling water, was replaced by the other bent tube when experiments were carried out at the temperature of boiling aniline. The deflexions obtained at the various temperatures are given in Table VI.

---

[*] *Loc. cit.*

TABLE VI.

Temp. of Mercury 15° C. Deflexion in mm.	Temp. of Mercury 99° C. Deflexion in mm.	Temp. of Mercury 15° C. Deflexion in mm.	Temp. of Mercury 180° C. Deflexion in mm.
10·5	14·5	11·3	19·0
10·5	13·5	11·6	17·3
10·5	14·5	11·6	16·3
10·5	14·3	—	17·3
10·7	14·2	—	16·3
—	12·6	—	19·0
—	12·9	—	16·5
—	14·8	—	—
—	13·8	—	—
—	12·6	—	—
—	13·0	—	—
Mean 10·54	Mean 13·7	Mean 11·5	Mean 17·4

According to the above table, $\dfrac{\delta R_{99^\circ \text{C.}}}{\delta R_{15^\circ \text{C.}}} = 1{\cdot}3$

and $\dfrac{\delta R_{180^\circ \text{C.}}}{\delta R_{15^\circ \text{C.}}} = 1{\cdot}51.$

The approximate values* of $\dfrac{\eta_{15^\circ \text{C.}}}{\eta_{99^\circ \text{C.}}}$ and $\dfrac{\eta_{15^\circ \text{C.}}}{\eta_{180^\circ \text{C.}}}$ are 1·3 and 1·51 respectively.

It is therefore concluded, within the limits of experimental error, that δR varies inversely as the viscosity. This is the result to be expected if the motion set up in the tube is steady.

---

* Kaye & Laby's Tables of Physical Constants, p. 30.

Experiments carried out with two straight tubes of different diameters.

Two tubes of diameter ·96 and ·5 mm. respectively were placed in almost exactly the same position with respect to the magnetic field, and the values of the deflexions for each tube determined for a current ·066 ampere and a field of 10,000 gauss. The resistances of the two tubes were ·36 and ·99 ohm, and their lengths 27 and 20 cm. respectively. The leads were out of the field, and, as previously shown by Jones *, the effect for straight tubes is independent of the resistance in the field. The experiments were carried out under conditions of steady motion $\left(\frac{\delta R}{h^2} = \text{constant}\right)$, and it was found impossible to obtain reasonably accurate results with tubes of smaller diameter than ·5 mm., as the deflexions obtained were too small. Jones † had previously investigated the effect of varying the diameter in the case of wide tubes carrying large currents $\left(\frac{\delta R}{h^{1\cdot 58}} = \text{constant}\right)$, and found that δR was proportional to the diameter. The results obtained for the two tubes are given below in Table VII.

TABLE VII.

Current in amperes.	Field in gauss.	Tube of diam. ·96 mm. $\delta R \times 10^6$ ohms.	Tube of diam. ·5 mm. $\delta R \times 10^6$ ohms.
·066	10,000	24·19	12·24

The results show that δR increases with the diameter of the tube, and that it varies approximately as the diameter of the tube.

The Effect of a Magnetic Field on the Resistance of Amalgams.

In the first series of experiments the increase of resistance produced in pure mercury was compared with the increase produced in an amalgam containing 0·5 per cent. of bismuth.

Bent tubes were employed in these experiments, and after measurements had been made for pure mercury, the tubes were filled with the amalgam and replaced in exactly the same position. After the observations had been completed in the case of the amalgams, the tubes were again filled with pure mercury and the first set of measurements were repeated. Experiments of a similar kind were carried out with straight tubes filled with pure mercury, an amalgam containing 0·64 per cent. of bismuth, and an amalgam containing 1·187 per cent. of zinc. The results obtained are given in Tables VIII. and IX.

---

* *Loc cit.*

† *Loc. cit.*

TABLE VIII.

Bent tube of diameter 1·1 mm. containing Mercury and Bismuth amalgams.

Field h in gauss.	Pure Mercury.			Amalgam containing 0·5 per cent. Bismuth.		
	Deflexion in mm.			Deflexion in mm.		
	·065 amp.	·13 amp.	·465 amp.	·065 amp.	·13 amp.	·465 amp.
10,000	10·75	21·8	61·2	10·55	21·1	60·4
7,904	...	13·6	...	...	13·75	41·35
7,071	5·25	10·9	...	5·3	11·35	32
4,814	2·42	5·2	...	2·5	5·15	14·9

TABLE IX.

Straight tube of diameter ·96 mm. containing pure Mercury, Bismuth amalgam, and Zinc amalgam.

Currents in amperes.	Field in gauss.	Pure Mercury. Deflexion in mm.	Amalgam containing ·646 per cent. of Bismuth. Deflexion in mm.	Amalgam containing 1·187 per cent. of Zinc. Deflexion in mm.
·068	10,000	4·9	4·76	4·59
·279	10,000	17·5	17·2	16·7

These experiments show that, within the limits of experimental error, there is no appreciable difference between the increase of resistance in the case of pure mercury and the amalgams examined. If the effect measured is due entirely to the motion of the liquids, the increase of resistance should be less in amalgams than in pure mercury, owing to the increase of viscosity produced by solution of a metal in mercury. According to the measurements of Feninger [*], the viscosity of 0·64 per cent. bismuth amalgam is 1·08 per cent. greater than that of pure mercury. It therefore follows that the deflexion for small currents (·068 ampere) when the motion is steady should be 1·08 per cent. less than for pure mercury, and the difference should become less for higher currents when the motion is turbulent. The difference due to change of viscosity is, however, too small to be measured with accuracy for the bismuth amalgams of the concentrations employed in the present experiments. The viscosity of 1·187 per cent. zinc amalgam [†] is 6·54 per cent. greater than that of pure mercury, and the deflexions obtained for small currents should be 6·54 per cent. less than for pure mercury. The evidence seems to indicate that there is a small diminution in the increase of resistance produced by the field when bismuth and zinc are dissolved in mercury. The experiments support the view that the increase of resistance produced in amalgams by a transverse magnetic field is due to motion produced in the amalgams ; and the results are not of sufficient accuracy to decide if the solution of bismuth or zinc in mercury produces a very small real effect of the same type as observed in solid metals. A very small effect of this kind may possibly be superimposed on the much larger effect due to motion.

Experiments with flat glass cells of rectangular cross-section.

Some experiments were carried out on the increase of resistance produced in mercury contained in flat glass cells of rectangular cross-section. When the depth of the cell is large compared with its width, the effect seems to be more complicated than for tubes of circular cross-section. If the depth of the cell is made equal to its width, so that the cross-section of the mercury column is a square, the laws followed by mercury when contained in a tube of circular cross-section are obeyed.

---

[*] Feninger, "Die Elektrische Leitfähigkeit und innere Reibung verdünnter amalgame." Inaugural Dissertation, Freiburg, 1914

[†] Feninger, *loc. cit.*

Further experiments will be carried out on this problem.

Summary of Results.

1. Experiments were carried out on the increase of resistance of mercury contained in bent and straight tubes for values of the current ranging from ·03 to 1·4 amps., and for fields ranging from 3,000 to 10,000 gauss.

2. It was found for tubes having diameter of about 1 mm., and for small currents, that the increase of resistance is independent of the current passing through the tubes, and is proportional to h^2.

3. As the magnitude of the current passing through the mercury increased, the change ef resistance δR became dependent on the current until finally (for the maximum current employed in these experiments)

$$\delta R \propto \frac{h^{1\cdot 58}}{i^{\cdot 4}}.$$

4. The effect of temperature on the change of resistance was also investigated, and it was found that the increase of resistance for small values of the current varied inversely as the viscosity.

5. The results obtained are in agreement with a theory put forward by Williams, who assumes that the increase of resistance is due to the production of motion in the mercury and amalgams by the action of the magnetic field.

6. The increase of resistance was examined for two straight tubes of diameter ·96 and ·5 mm. respectively, and it was found to be approximately proportional to the diameter for small values of the current passing through the mercury column.

7. The increase of resistance produced in amalgams containing 0·5 and 0·64 per cent. of bismuth and an amalgam containing 1·187 per cent. of zinc was measured, and it was concluded for the concentrations employed that the solution of either bismuth or zinc in mercury produced no appreciable change in the increase of resistance. The experiments showed a slight diminution in the change of resistance produced by the magnetic field when bismuth and zinc are dissolved in the mercury. This result is to be expected on the theory that in conducting liquids the

increase of resistance is not a true effect, but is produced by the motion set up in the liquid.

This motion is less in amalgams than in pure mercury, as the viscosity of the former is greater.

These experiments were carried out in the physics laboratories of the University College of Swansea under the guidance of Professor E. J. Evans, and we thank him for his valuable suggestions and constant advice.

We also thank the Department of Scientific and Industrial Research and the Glamorgan County Council for grants which made this research possible.

January 1926.

XIV. *The Analysis of the Copper Spectrum.*
By W. M. Hicks, *F.R.S.*[*]

I. The Linkage Systems and the Rydberg Separations.

ALTHOUGH the existence of links was first made evident during a discussion of the copper spectrum, the linkages of Cu have not hitherto been considered in detail. The present communication is confined to the discussion of these linkages and includes an attempt to fix the origin and the nature of the Rydberg separations[†]. It is hoped in a later paper to deal with certain aspects of the series relationships, especially in the light of two recent important papers by Shenstone[‡] and by Stücklen[§].

1. It should be remembered that every link enters as the difference of two comparatively near term levels. We may indeed imagine that in the violence of the spark excitation a recombining electron may give some of its excess energy to the other electrons round the nucleus. We may picture the process as first a set of shocks to each electron or some of them round the nucleus, displacing them and altering

---

[*] Communicated by the Author.

[†] I have been criticised because in my various papers on the analysis of spectra I do not refer to the generally accepted views as to the detailed way in which the electrons outside the nucleus are arranged or move. But my aim has been not to illustrate a theory—or to criticise it—but to examine the spectral data themselves and try to discover their interrelations and the laws on which they are built up. Many of these are of great simplicity, and they ought to be taken account of by those specially working on general theory.

[‡] Phil. Mag. xlix. p. 951 (1925).

[§] *Zeit. f. Phys.* xxxiv. p. 562 (1925).

their energies. But the new configurations may not be those governed by quantum considerations. Consequently in their accelerations they dissipate a portion of their energies until they fall into a quantum configuration (*i. e.*, a non-dissipating one) near their original paths. Next they fall into their original states and pass on their freed energy to the nucleus to be radiated according to quantum laws. The different levels in each case may be those of a complex term (different j, same k) or in general may be certain others not usually occupied in the normal or quiet transitions, but which we can calculate with very great exactness so soon as we know the usual series limits and separations. Again, when one level, or the two levels, of a quietly transiding electron is modified we get displaced lines. Such for instance are the origins of the various series and satellite separations which may be called normal displacements. Summation lines (almost wholly spark lines) must have a completely different origin. Until we know their source we may provisionally suppose that they are due to the existence of a doubly ionized atom simultaneously neutralized by two electrons, one going to the limit term level and the other stopping momentarily at a higher term level. *E.g.*, we might suppose $\mathbf{S}(3)$ or $p(1)+s(3)$ to be due to the presence of the $++$ atom simultaneously neutralized by one electron falling in to the $p(1)$ level and the other to $s(3)$. Naturally in all these cases simultaneity would never happen, and we should have to imagine that some short interval is required in settling down *or* that there is some short interval between the complete transmission of energy from the electrons to the nucleus and its emission as radiation by the latter.

The existence of linked lines shows that the general supposition that all spectral lines are due to the difference of two terms only is too restricted. Many such in the long lists of new terms in elements which have been published by several investigators lately possibly contain many spurious ones due to this belief. Even negative terms have been admitted which should correspond to impossible* finite orbits whose total energy is greater than that from infinity. For instance, in the summation example above of $\mathbf{S}(3)$ the second term would be regarded as a negative one. But such an explanation is merely verbal and can correspond to no reality. The idea that a line might be represented as the sum or difference of the frequencies of two other lines

---

* That is, if any magnetic action of the nucleus is neglected, as is usually done in current theory.

O 2

(*i. e.* dependent on four terms) is not a new one. Moggendorff[*] indeed attempted to give examples of such, although unfortunately all his instances reduced[†] in reality to the difference of two terms only.

2. For data we have very accurate measures between 8680 and 6740 by Meggers[‡]. He gives estimates of his probable errors varying from ·01 to ·05. Below 6740 the measures of Hasbach[§] are used except that in the region down to 5000, where he has observed comparatively few lines, the observations of Aretz[||] are used and in the sparse region of arc lines from 5700 to 5000 spark lines, chiefly by Eder and Valenta[¶], have been taken into consideration. Exner and Haschek[**] have also noted many extra arc lines, some of which have been made use of. The original observations of Kayser and Runge are now replaced by the very accurate ones of Hasbach, working in Kayser's laboratory. He reads to three places of decimals in the majority of his lines, and in *general* his observation errors may be taken as not greater than a few units in the last place. That this is so may be inferred by comparison with other observers, who in special cases have observed single Cu lines also to three places. Some examples are given below in connexion with his complex lines. Aretz also observes to three places, but for reasons given by Hasbach they are often in error by one or two units in the second place. His separations of near lines, however, are not affected to the same degree.

The Satelloid Group.

3. Hasbach gives a considerable number of strong lines as complex, exhibiting numerous companions ("trabanten"). The laws of the separations of the companions of complex lines are little known. The separations are generally small and do not depend like the series separations on oun displacements. The separations of Hasbach's lines are larger than those of complex lines in general. Janicki gives only four lines as complex, viz. the two inverse D'_{12}, D'_{22} lines where Hasbach has none and the other two in common with him, but with smaller separations. We might almost suspect them to be the result of a Stark effect were it not for their

---

[*] *Proc. Kon. Akad. Wetens. Amsterdam*, Dec. 1911.

[†] 'Analysis of Spectra,' p. 37.

[‡] Bull. Bureau Stand. Wash. No. 312 (1918).

[§] *Zs. wiss. Phot.* xiii. p. 399 (1914).

[||] *Zs. wiss. Phot.* ix. p. 256 (1910).

[¶] *Denks. Wien. Akad.* lxiii. p. 189 (1896): data taken from Kayser, Bd. 5. Referred to as E.V.

[**] *Spek. der El. bei normalem Druck*, 1911, 1912. Referred to as E.H.

irregularity and the fact that none of them appear in D lines. So also the irregularity of the spacings and the fact that near lines of the same character do not show them would seem to exclude the supposition that they are due to ghosts; *e.g.*, whereas (4) 3208, (6) 3194 show them, the near lines (4) 3231; (6) 3142; (6) 3126 do not. Moreover, the linkage maps, as we shall see, show that they belong to one related system—a strong indication that their source must be looked for in term properties and not in grating deficiencies. They are not satellites as ordinarily understood, and I shall refer to them as satelloids. They show certain peculiarities which are important for our present purpose as well as for their experimental illustration of known link properties. They deserve a preliminary discussion. Quite recently Stücklen * has observed satellites, but more numerous, in the same lines. She does not, however, give measures and does not appear to be aware that Hasbach had already observed them. The whole set are given in the following list. The intensities are of the order 6 ± 2.

Table I.

1 (5, VIII.).			
4704·598[1]	21249·87		y
04·20	51·67	1·80	$3y=1·71$
2 (7, VIII.).			
2·30	88·75	5·40	$9y=5·13$
1·986	90·20	3·95	$7y=3·99$
4651·130[2]	21494·15		y
0·73	96·00	1·85	$3y=1·71$
0·3	97·98	3·83	$7y=3·99$
		9·23	$16y=9·12$
3 (?)			
5·45	82·79	1·74	$3y=1·71$
4275·131[3]	23384·53		? y
4·79	86·42	1·91	$3y=1·71$
4 (51, VI.).			
3602·038	27754·18		y
01·75	56·39	2·21	$4y=2·28$
5 (16, VI.).			
0·67	15·18	2·26	$4y=2·28$
0·55	16·14	1·30	
3530·388	28317·44		y
0·252	18·53	1·09	$2y=1·14$
0·10	19·75	2·31	$4y=2·28$
		5·57	$8y=5·56$
6 (47, VI.).			
8·45	45·44	5·38	$10x=5·40$
8·11	48·49	2·33	$4y=2·28$
8·04	49·11	1·71	$3y=1·71$
3337·850	29950·82		y
7·73	51·90	1·07	$2x=1·08$
7·668	52·45	1·62	$3x=1·62$
7·571	53·32	2·50[4]	
		7·88	$14y=7·98$
7 (2, I.).			
8·55	16·06	5·45	$10x=5·40$
3307·952	30221·51		x

---

[1] Janicki gives triplet *dn* ·148; ·174.

[2] Janicki gives as single and very sharp.

[3] Have no attached links. Janicki gives doublet *dn* ·264.

[4] This is a $2\delta_1$ displacement on $p_1=2·47$. The total for the others is then 7·00 with $13x=7·02$; for more complete treatment see note 6 to Map VI.

* *Zsch. f. Phys.* xxxiv. p. 562 (1925).

TABLE I. (*continued*).

8 (3, II.).

3·09	50·36	3·48	$6y=3{\cdot}42$
3282·716	30453·84		y
2·33	57·42	3·58	$6y=3{\cdot}42$

9 (6, I.).

80·687	72·67	8·02	$15x=8{\cdot}10$
80·40	75·34	5·35	$10x=5{\cdot}40$
3279·823	30480·69		x
79·54	83·33	2·64	$5x=2{\cdot}70$
79·06	87·78	7·09	$13x=7{\cdot}02$
		15·11	$28x=15{\cdot}12$

10 (5, I.).

3208·236	31160·80		y
8·119	61·93	1·13	$2y=1{\cdot}14$
7·94	63·69	2·89	$5y=2{\cdot}85$
7·65	66·50	5·70	$10y=5{\cdot}70$

11 (17, II.).

4·66	93·23	5·44	$10x=5{\cdot}40$
4·34	96·36	2·31	$4y=2{\cdot}28$
3194·103	31298·67		x
3 979	99·89	1·22[5]	
3·81	301·35	2·68	$5x=2{\cdot}70$
		8·12	$15x=8{\cdot}10$

12 (8, I.).

3108·603	32159·49		x
8·43	61·55	2·06	$4x=2{\cdot}16$

13 (4, III.).

3093·993	32311·36		y
3·72	14·25	2·89	$5y=2{\cdot}85$

14 (5, III.).

3073·803	32523·58		x
3·704	24·62	1·04	$2x=1{\cdot}08$
3·53	26·35	2·77	$5x=2{\cdot}70$

15 (30, II.).

3063·416[6]	32633·84		x
3·18	36·35	2·51	$5x=2{\cdot}70$

16 (3, III.).

3036·105	32927·38		y
5·89	29·72	2·34	$4y=2{\cdot}28$
5·84	30·26	2·88	$5y=2{\cdot}85$

17 (notes to III.).

2997·363[7]	33352·97		x
7·13	55·57	2·60	$5x=2{\cdot}70$

18 (10, III.).

1·76	54·38	6·15	$11y=6{\cdot}27$
2961·177	33760·53		y
0·92	63·48	2·95	$5y=2{\cdot}85$
		9·10	$16y=9{\cdot}12$

19 (?)

3·18	73·78	2·92	$5y=2{\cdot}85$
2882·937[8]	34676·70		
2·713	79·40	2·70	$5y=2{\cdot}85$
		5·62	$10y=5{\cdot}70$

---

[5] This is one oun on p.

[7] See note 4 to map III.

[6] Is Shenstone's $d_2' - p_f$.

[8] Has no links—is Shenstone's Y-- p_f

The first column gives wave-lengths, the main line being in full; the second wave-number; the third and fourth are explained below. The brackets following the ordinal number refer to the maps in which the lines occur.

To illustrate the degree of accuracy of Hasbach's measures referred to above, the readings of other observers for some of the lines in the table are here appended.

	1.	3.	4.	5.	6.	7.	11.	16.	18.
Hasbach	·598	·131	·038	·383	·850	·952	·103	·105	·177
Offermann	·605	—	·035	·385	·851	·950	·106	·107	·186
Hamm	·597	·132	—	·390	·848	·950	...	·103	·180
Josewski.........	—	·136	·045	—	—	—	·108	—	—
Vahle	—	—	·037	—	—	—	—	—	—

A similar result obtains if the numerous other cases given in Kayser's *Handbuch* are examined. I find only one case of real deviation, in which for Hasbach's 2441·625 Hamm gives ·665, Krebs ·651, E.H. ·67, and Huppers ·67. The deviation is so excessive that we must take it as a printer's or MS. error and that his true reading is ·665. We may feel some certainty, therefore, that his observation errors are in general less than ·005 when he reads to ·001.

If we examine the separations of the satelloids from their main lines, we shall see that they are practically all multiples of one of the two quantities $x = {}·54$ or $y = {}·57$, and that this is specially marked if we consider the separations of the extreme satelloids. Compare for instance their values for (5, 6, 9, 10, 11, 16, 18, 19). The intermediate satelloids are in general in good agreement with this rule, but they show slight indications of small shifts of pairs such as might be explained by a small Stark effect. The close agreement, with the large multiples involved, is extraordinary and shows that the effect is real. This sense of reliability is increased if the cases where a satelloid is measured to ·001 are considered. This dependence on multiple shifts, now to be regarded as established, is important as a sure evidence that the satelloid sets are all due to displacements in some one term (or two, if x is really different from y). In other words, all the lines involved must contain some common term in their formulæ. This conclusion is supported, as we shall see below, by the linkages which definitely relate the majority of these satelloid sets to P (1) lines. They are also closely associated with the maps in which Rydberg's 680·11 and 212·23 occur. We may suspect, then, that all these lines should really depend on P (1). Amongst others (15, 19) would then suggest that Shenstone's p_f are composite terms involving $p_1(1)$ or $p_2(1)$. The origin of the y shift must remain at present undetermined. If the satelloids are of the same nature as that of the close companions of strong lines, we should not expect the shifts to be due to oun displacements on a single term, and indeed such small shifts could not be produced in either of the terms $s(1)-p(1)$. The oun shift on $s(1)$ is 3·43 which is $6y = 3·42$, but this must be merely a curious coincidence for fractional ouns are inadmissible.

Stücklen has attempted to explain the satelloids as being of a band-like nature caused by the association of an atom with another very slightly bound one.

The existence of these satelloids is of extreme importance on another ground, in that they afford direct experimental evidence for the link modifications. We already know that as a fact when two lines are linked, their separation often differs slightly from that of the actual link. A link attached to a line A will indicate a line close to B, but this line may not be observed, and in general we find, when the terms involved are known, that B is displaced from its theoretical value by definite displacements in these terms. The evidence for this effect is definite[*]. The interest of these sets of Hasbach's just lies in the fact that in very many cases the satelloids give these theoretical lines. The discussion is best deferred until the linkage maps have been considered and it is taken in § 8.

The Linkages.

4. In its linkage systems copper is anomalous in that linked lines are found in the arc spectrum itself and not, as in other spectra, only to spark lines. In silver and gold no links are found within the spectrum as produced in the arc, although of course the various chains start from series or other definite non-ionized atomic lines. The usual links for Cu as given in a previous communication[†] are, when corrected to IA,

$$a=245{\cdot}54\ ;\quad b=248{\cdot}44\ ;\quad c=251{\cdot}39\ ;\quad d=254{\cdot}39\ ;$$

$$e=999{\cdot}80\ ;\quad u=680{\cdot}63\ ;\quad v=692{\cdot}08.$$

These can only be indeterminate within one or two units in the last decimal. The *a* ... *d* links in Cu differ so slightly that we shall make small use of them in the present discussion, chiefly because it is difficult to determine whether separations near their values are real links, or direct displacements, or pseudo-separations such as we get between D_{11} and D_{22} lines with near satellites not visible. Their existence, however, is evident on any preliminary testing of the spectrum, and they are the origin of the large number of separations near that of the doublets to which Rydberg[‡] first drew attention nearly thirty years ago. As is well known, he brought to light numerous sets of new separations about 680, 212, 130, and 50 for which he could give no explanation. We shall refer to the three latter categories as X, L, M. He arranged some of these (shown with thicker connecting lines in map VI.) in a peculiar form of multiplet of a kind which he says "I have never observed before." His 680 is of course the *u*-link, but the others still remain to be explained. A first step is to get some idea of their exact values and degree of variation. For this purpose their occurrency curves have been determined. They are given in the accompanying diagrams. In these each dot represents an observed separation equal to the corresponding abscissa ±·05, whilst the ordinates give the number of cases within ±·2 of the abscissa value. A rather wide extent of variation was taken in the test as their actual values were unknown beforehand. The curves show at a glance that the X separation has a maximum occurrency about 212·3 with minor maxima about 210·2, 214, and possibly near 211·4, but the peak at 211 would largely disappear if the ordinates were taken =abs.±·01 instead of ±·02. The L show a maximum near 129·5 and a minor one near 130·5, but the broad peak round 129·5 shows that there are a large number between 129·3 and 129·8. In sharp contrast to these the M shows a very great rise near 50·3 and no other, but again a considerable number within 50 to 51. The individual separations almost certainly have errors < ·1, so that where they crowd together the majority should be regarded as real X, L, M, whilst of the sparse ones many may be merely numerical coincidences.

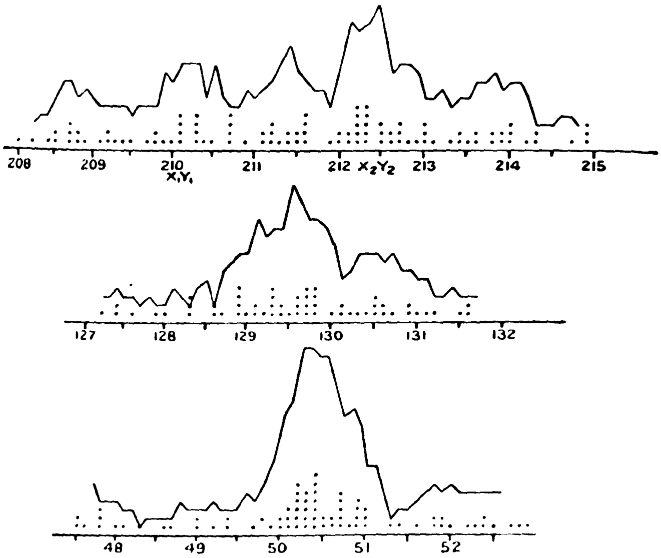
---

[*] For a few illustrations see my 'Analysis of Spectra,' pp. 153-6, 159-161.

[†] Phil. Mag. xxxix. p. 462 (1920).

[‡] Astro. J. vi. p. 239 (1897).

Fig. 1.



The linkages which emanate from the recognized series lines have been represented in maps, in which some latitude has been allowed in the new Rydberg separations. These maps are simply the raw material on which to base conclusions. It is not to be supposed that the lines are actually built up one after another in the way indicated in a map or are related to a system such as the ordinary series lines which depend on a regular sequence. Each line is an independent set of link modifications superposed on the two fundamental series terms of the map involved. There is even no *à priori* reason why we should expect identical line characters in differently linked lines, such as we might perhaps expect in similarly displaced lines. The map is a means of identifying them, and even if the inclusion of a particular line is inadmissible it may yet serve as a stepping-stone between for the discovery of others.

The details of each map are discussed in the notes to each. To save space a line is represented by a small circle with an included number referring to the accompanying list. The exact separations are entered in thick type. Where there are definite reasons for disallowing a separation as a true link, it is enclosed in [ ]. In order to guard against assertions that the observed separations are merely coincidences in a crowded spectrum, the separations of each line from the nearest observed line on each side are given in small figures, except where a — means that the next is a succeeding linked one. In a few cases excessive deviations from the values in the occurrency curves have been admitted where their reality has been suggested by neighbouring regularities.

The large number of exact separations of 680·11 or close to it is very noticeable in those maps which include lines of Hasbach's satelloid group, and which also are connected to the P(1) series lines. It is ·52 less than the normal u-link which suggests the $y=\cdot57$ displacement. The difference ·05 is equivalent to an observational error $d\lambda < \cdot005$, which is within our permissible limits, but the large number with the same value may raise some doubt. It will, however, be treated as a u-link with concurrent displacements.

If these maps be examined, paying regard to the separations from neighbouring lines, indicated by the attached small figures, it will be seen that the great majority are well isolated from others and consequently that the large number of examples of the new separations really represent some definitely related system, even although their values differ considerably from equality, especially in the L, M sets. This reality is also emphasized by the numerous examples of the appearance of the L, M in similar collocations. The maps reproduce the well-known features of the *e*, *u*, *v* linkages, which need not now detain us. Details will be found in the notes appended to each map. It is, however, interesting to notice that in these Cu-linkages the *u*-links greatly predominate over the *v*. There are also a large number of examples of series inequalities, such as for example the first two links from $P_2(1)$ in map I. of $(-e-{\cdot}17)+(u+{\cdot}17)=-e+u+0$ ending in the satelloid of (2), or again $680{\cdot}11+681{\cdot}02=2(u-{\cdot}06)$. We pass on to the immediate problem, that of the nature and origin of the X, L, M separations.

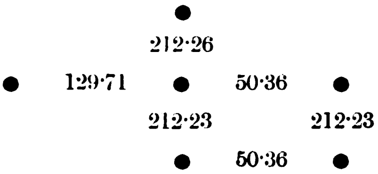
5. In discussing the origin of these, three suppositions are at our disposal, in the light of present knowledge :—

1. They are analogous to ordinary multiplet separations (different *j*-quanta), *i. e.* involve new "terms".
2. They are links formed in some way analogous to those already known.
3. They have their origin in displacements or successive displacements in one of the main terms entering into the lines involved.

If they are analogous to multiplet separations, these generally form an arithmetical progression. Landé's rule goes further and may be stated in the form that they should be proportional to a series of numbers differing by 2 and starting from some particular integer. In other words if $s_1, s_2 \ldots$ denote the separations they form an A.P. with common difference s_2-s_1, and in Landé's rule the first number $=2s_1/(s_2-s_1)$. Now the separations in question do form an A.P. with common difference about 80. On Landé's rule the first number should be $100/80=1{\cdot}25$ and is not even an approximate integer. His rule would therefore exclude supposition 1, but his rule is only an approximate one. Nevertheless, consideration of Rydberg's "remarkable multiplet" shown with thickened connexions in map VI., 2, 3, 4—5, 6, 7—8, 9, 10, will show that they cannot all thus enter.

Moreover, from our present knowledge we infer that if they form a set of triplets, the sets must belong to the ionized ion. In that case they would not be associated with links dependent on the neutral atom, as in fact they are.

Again, the essential property of all known multiplets is that the separations appear as pairs which are never repeated as pairs in the same multiplet. In fact this is the experimental basis for the "principle of selection" in *j*. It follows, therefore, that the 680·11 must be of a link nature quite independently of its close relation in value to the known u. The (5, 6, 7, 10) may then be put aside as merely sets parallelized by the u-link. The others with (11) added may be arranged thus:—



This indicates that if there is an analogy with doublets and triplets, the 212 must depend on one term and the other two 129, 50 on a second. So far as this particular set of lines is concerned, this may be the case for 129, 50, but it cannot be the case for 212. The various values for each 212 are extraordinarily close. We find two successive separations 212·26, 212·23 clearly really equal, and this cannot occur with successive displacements in the same term, for the same displacement must give a shift differing by more than ·03. This points to the supposition that the 212 are of the nature of links. It is easy to see also that 212 must be some link, and that 130, 50 cannot be displacements on one and the same unmodified term as in the ordinary series separations, since we find numerous cases of successions of separations near their values. If they are displacements in some term, they can only occur if that term is present. Now a search will show that 212 appears connected with known difference lines involving terms of all the known types. On the other hand, we do not find the 130, 50 connected with lines in which we can be certain that the term $p(1)$ does not occur and that they are numerous where it does. We will therefore consider the 212 sets and the 130, 50 separately.

The 212 sets.

6. Confine ourselves for the present to separations near 210·2, 212·3 quite definitely given by the occurrency curve. We get a few in the direct P linkage of map II. and some striking sets in the parallel chains of map III. A few occur in IV. (S 2), several in V. (D′ or inverse D), very numerously in VI. (probably P 1), many in VII. (probably composite) and in VIII. (portion ? to P). 210·68 is linked to Randall's X[*]$-p_12$. My suggestions of $Q_1(1)$, $Q_2(1)$

---

[*] X is Randall's symbol x for what Shenstone calls d_21, and Y represents the latter's d_11.

have respective links of 208·7, 212·7. $Q_2(2)$, Shenstone's $s(1)-p_e$, has 209·50; 24643 or p_1-f3 has 208·47; 21282 ($?\,d_2 1-d_1 3$) has 212·58. Of Shenstone's combinations, $s(1)-p_d$ has 214·03, 212·10 in series, $Y-p_c$ has 212·63, 209·26 in series, $X-p_c$ has $u-210{\cdot}50$, $X-p_f$ has 211·11. It is attached also to some of the lines of Stücklen's multiplets and to many others not yet allocated. The above list contains lines depending on $s(m)$, $p(m)$, $d(m)$, $f(m) \,.\, d_2'1 \,.\, Y$, and other terms. The separation then cannot arise from a term already present and must be of the nature of a link. That being accepted, the question arises as to its source. The $a \ldots d$, e links arise from $\pm\Delta$ displacements on $p_1 1$, $p_2 1$, the u, v from $\pm\Delta$ displacements on $s(1)$. It lies to hand, therefore, to test whether they arise from $\pm\Delta$ displacements in some other term. Naturally the first term to test is $d(1)$. The satellite separation of $d_1 1$, $d_2 1$ is very close to 27 and may be slightly larger, but the uncertainty will not appreciably affect the values. The values of $d_2(1)$ and $d_1(1)$, as well as their mantissæ, were given in R.A. in a paper † about six years ago. The values corrected to I.A. are

$$d_2(1) = 28415{\cdot}50 = N/(1{\cdot}964642)^2,$$

$$d_1(1) = 28388{\cdot}01 = N/(1{\cdot}965592)^2,$$

with $$\Delta = 7306{\cdot}9,$$

and we have to calculate the values of $d_2(1)(\pm\Delta)-d_2(1)$ and $d_1(1)(\pm\Delta)-d_1(1)$. Denote the values on d_1 by X and on d_2 by Y; X_1, Y_1 for the $+\Delta$ links and X_2, Y_2 for the $-\Delta$. *E.g.*,

$$X_1 = N/(1{\cdot}965592+7307)^2 - N/(1{\cdot}965592)^2.$$

The values calculated are

$$X_1 = 209{\cdot}88, \qquad Y_1 = 210{\cdot}21,$$

$$X_2 = 212{\cdot}27, \qquad Y_2 = 212{\cdot}54.$$

The agreement with our observed values is strikingly close. We have seen how in the occurrency curves the observed values crowd together round 212·3 and 210 with a very large number $= 212{\cdot}3 \pm {\cdot}2$. There can then, I think, be little doubt but that the 212 separations are links as calculated above. We thus discover a new fact in spectral laws of the greatest importance. Further support in favour of the X being links with the above values in Cu is afforded by a study of the maps which show a large number of series and parallel irregularities, a phenomenon distinctive of true linkages. We find, for instance, amongst others,

---

† Phil. Mag. xxxix. p. 463 (1920).

$$\begin{aligned}
\text{Map II.}\quad & 208{\cdot}54+211{\cdot}11 = 2X_1-{\cdot}03\\
\text{III.}\quad & 211{\cdot}73+212{\cdot}69 = 2X_2-{\cdot}12\\
& 212{\cdot}18+680{\cdot}71 = X_2+u-{\cdot}01\\
\text{V.}\quad & 213{\cdot}61+208{\cdot}86 = 2X_1-{\cdot}01\\
\text{VI.}\quad & 1001{\cdot}23+210{\cdot}71 = e+X_2-{\cdot}13\\
\text{VII.}\quad & 210{\cdot}56+214{\cdot}63 = 2Y_2+{\cdot}10
\end{aligned}$$

7. If the law is general, indications of similar links should be expected in other elements, especially in Ag and Au of the same group. On account of its great importance in general theory, a preliminary test on the arc lines of Ag and Au has been made. The *d* (1) data for silver [*] and gold [†] were given in former papers in this Magazine. They are reproduced here with the values of X, Y now calculated therefrom :—

	Ag.	Au.	
Δ	27789·1	113935	
δ	421·04	1406·7	
Sat. displ.	23 δ_1	28 δ_1	
d_2	28997·41 = $N/(1{\cdot}944829)^2$;	26735·85 = $N/(2{\cdot}025415)^2$	
d_1	28925·33 = $N'(1{\cdot}947250)^2$;	26477·75 = $N/(2{\cdot}035262)^2$	
X_1	808·22	2732·90	*·81* R.A.
X_2	843·61	3233·39	*·29* "
Y_1	811·24	2771·92	*·83* "
Y_2	846·76	3282·19	*·08* "

The arc spectra of these metals were then tested for separations of about these values, confining attention only to links from arc lines. No complete investigation has been made and only the arc lines as given by Kayser and Runge and by Kaspar were used, about 70 in Ag between 17638 and 44500 and about the same in Au. The linked lines now, however were sought for in their natural habitat of the spark spectrum. The result is given in the following lists, the values for Au being in R.A., an old hand-list in R.A. being at disposal. The observed separations are in thick type, and those of neighbouring spark lines are inserted in ( ), as in the maps.

---

[*] Phil. Mag. xxxviii. p. 316 (1919).

[†] *Ibid.* xxxviii. p. 8 (1919).

Ag.

1.	(18, 15)	17932·14	**812·57**	18744·71	$(-D'_{11}1)$			
2.	(30·18)	17913·90	**843·57**	18757·47				
	(15, 38)	46·89	**810·58**					
3.	(14, 86)	18342·73	**849·18**	19191·91	$(D_{22}2)$			
4.				21943·15		**808·75**	22751·90	(271, —)
						855·25	98·40	(—, 14)
5.				24652·33[1]	$(D_{22}3)$	**850·68**	25503·01[2]	(89, 10)
6.	(37,23)	26392·4	**842·0**	26234·48	$(D_{11}4)$	**851·64**	27086·12	(29, 54)
7.				26941·61	$(S_1 5)$	**857·7**	27799·3	(126, 121)
8.				27584·4	$(D_{11}5)$	**853·**	28437	(420, 18)
9.	(62, 181)	27209·38	**851·14**	28060·52				
10.	(29, 126)	27672·70	**847·31**	28520 01				
11.				28547·47		**811·50**	29358·97	(66, —)
						842·51	89·98	(-, —)
						853·90	29401·37	(—, 23)
12.				29551·79	$(P_2 1)$	**811·60**	30363·4	(5, —)
						842·14	93·93	(—, 11)
13.	(15, 61)	29231·58	**810·47**	30042·05				
14.				30241·03				
				846·95				
	(22, 20)	30279·75	**808·23**	31087·98		**844·5**	31932·5[3]	(116, 17)
				850·87				
				31938·85	(see 17)			
15.				30472·90	$(P_1 1)$	**848·0**	31320·9	(17, 40)
16.	(10, 11)	30679·3	**851·8**	31531·09				
	(8, 10)	30723·5	**807·6**					
17.	(36, 16)	31126·7	**812·1**	31938·85		**810·57**	32749·42	(128, 61)
	(12, 36)	31089 86	**849·00**					
18.	(15, 15)	31445·65	**812·34**	32257·99				
19.				36728·95		**846·86**	37575·90	(56, 39)
				848·76				
20.	(114, 23)	36767·4	**810·3**	37577·69				
21.				38818·93		**804·2**	39623·1	(38, 28)
22.	(23, 14)	40202·62	**807·71**	41010·33		**807·75**	41818·08	(43, 65)
23.	(18, 14)	40618·63	**809·56**	41428·19[4]		**845·4**	42273·6	(16, 12)→
24.	(16, 12)→	42273·6	**811·8**	43085·39		**810·26**	43895·65	(27, —)
						850·95	43936·34	(41, 22)
25.				43147·41		**811·34**	43958·75	(21, 27)
26.	(22, 11)	43005·71	**842·67**	43848·38[5]		**812·65**	44661·01	(40, 94)
27.				44458·68		**806·57**	45265·25	(55, 52)
28				44503·72		**845·29**	45349·01	(31, 17)

[1] Kaspar gives 24650·75.

[2] By E.H. E.V. give ... 04·18.

[3] E.H. observe this and 31939·6.

[4] 809·56 + 854·4 = $X_1 + Y_2$ a series inequality.

[5] 842·67 + 812·65 = $X_1 + Y_2 + \cdot 34$ " "

Au.

1.				15791·60	**2777·81**	18569·41	(38, 8)
2.				15923·38 $(-D'_{22}1)$	**3290·34**	19213·62	(100, 207)
3.				17050·97	**2777·67**	19828·64	(90, 100)
4.				19113·51 $(-D'_{11}1)$	**2732·90**	21846·41	(8, 14)
5.	(30, 21)	18011·59	**2764·91**	20776·50 $(S_1 3)$			
6.	(11, 28)	17573·91	**3285·06**	20858·97 $(D_2 2)$	**3275·51**	24134·48	(60, 79)
7.	(17, 35)	18155·67	**3277·75**	21433·42	**3232·85**	24666·27	(50, 73)
8.	(125, 7)	18415·80	**3285·87**	21701·67	**3281·41**	24983·08	(6, 29)
	(18, 12)	18467·56	**3234·11**	**2775·79**			
				24477·46 (see 14)			
9.				22273·24	**2772·15**	25045·39	(33, 10)
					3228·05	25501·29	(16, —)
					3235·85	09·09	(—, 19)
10.				22529·32 $(D_{11}3)$	**2770·87**	25308·19	(59, 29)
					3284·53	25813·85	(14, 9)
					3234·35	25763·77	(21, 19)
11.				22904·68	**2771·90**	25676·58	(14, 6)
					3225·93	26130·61	(18, 18)
					3290·06	26194·74	(27, 15)
12.	(75, 310)	20392·38	**2774·49**	23166·87	**2735·84**	25902·71	(28, 20)
					2766·61	25933·48	(6, —)
					2774·61	41·48	(—, 42)
					3229·36	26396·23	(61, 28)
					3279·90	26446·77	(22, 34)
13.				23567·34	**2767·78**	26335·12	(23, 61)
					3228·23	26795·57	(13, 47)
					3274·69	26842·03	(47, 46)
14.				24477·46	**2724·98**	27202·44	(11, 8)
					33·20	10·66	
					3234·12	27711·58	(6, 20)
					3281·19	27758·65	(27, 25)
15.	(21, 27)	21365·24	**3226·83**	24592·07 $(S_2 3)$	**2737·27**	27329·34	(28, 5)
	(9, 20)	21818·29	**2773·78**		**2770·11**	27362·18	(5, 20)
	(14, 11)	21860·79	**2731·28**		**3281·26**	27873·33	(40, 40
16.	(45, —)	21973·73	**2765·33**	24739·06	**2775·65**	27514·71	(13, 5)
	(—, —)	22001·67	**2737·39**		**3233·44**	27972·50	(17, 62)
	(—, 89)	22013·58	**25·48**				
17.				25571·39	**3235·01**	28806·40	(11, 152)
18.	(23, 221)	22874·60	**2772·21**	25646·81			
19.	(9, 21)	25396·77	**2734·92**	28131·69			
				3287·18			
				31418·87			
20.	(12, 7)	26105·71	**2728·01**	28833·72	**3237·19**	32070·91	(25, 109)
21.	(20, 13)	27382·63	**2726·51**	30109·14	**3236·20**	33345·34 ? Pt	(42, 32)
	(5, 21)	27334·57	**2774·57**				

Au (*continued*).

22.		…………	**3282·98**	30617·55			
	(20, 13)	27382·63	**3234·92**				
23.	(2, 39)	27444·78	**2772·63**	30217·41			
	(39, 18)	27483·17	**2734·24**	**2739·76**			
				32957·17			
24.	(7, 52)	28174·96	**2769·07**	30944·03			
	(46, 24)	27661·13	**3282·90**				
	(6, 20)	27711·58	**3232·45**				
25.	(40, 41)	27913·86	**8280·48**	31194·34			
26.	(22, 66)	28689·63	**2729·24**	31418·87			
27.		…………	**3280·58**	31970·13	**3280·24**	35250·37	(27, —)
					86·21	56·34	(—, 22)
28.				32904·37	**2769·66**	35674·03	(—, 85)
					2730·37	35634·74	(185, —)
29.				33001·33	**2775·19**	35776·52	(17, 172)
30.				33052·05	**3286·48**	36338·53	(390, 29)
31.				33165·51	**3276·71**	36442·22	(34, 136)
32.	(79, —)	30823·67	**2771·82**	33595·59	**2772·11**	36367·70	(29, 7)
	(—, 16)	28·51	**67·08**				
33.	(26, 38)	30498 87	**3230·89**	33729·76			
				3282·46			
				37012·22			
34.	(47, 11)	31017·94	**2731·98**	33749·92	**3276·15**	37026·07	(35, —)
	(54, 26)	30472·47	**3277·45**		**84·65**	34·57	(—, 22)
					3229·18	36979·10	(35, 12)
35.	(11, 23)	31028·43	**3283·24**	34311·67	**3278·08**	37589·75	(81, 118)
36.	(83, 103)	31669·32	**2732·64**	34401·96			
37.	(20, 26)	31941·23	**2728·26**	34669·49	**3278·72**	37948·21	(15, 39)
38.	(146, 16)	33147·81	**3227·06**	36374·87	**3230·21**	39659·88	(33, 56)
39.	(77, 46)	33729·55	**3282·67**	37012·22	**2735·16**	39747·38	(32, 54)
40.				37179·69	**3231·37**	40411·06	(39, 94)
41.	(28, 134)	34120·84	**3236·78**	37357·62 ($P_2$1)	**2765·64**	40123·26	(19, 17)
42.	(17, 76)	34567·63	**3277·08**	37844·71	**3233·34**	41078·65	(14, 6)
43.				38595·88	**2770·88**	41366·76	(12, 40)
44.				39291·95 F_1(2)	**2776·83**	42068·78	(15, 76)
					3281·17	42573·12	(62, 20)
45.	(12, 137)	36590·77	**3229·23**	39820·00	**2773·07**	42593·07	(20, 51)
46.				41172·94 ($P_1$1)	**3282·76**	44456·70	(8, 139)
47.	(86, 84)	39542·25	**2733·89**	42276·14	**2767·29**	45043·43	E.V. (25, 72)
					9·74	45·86	E.H.
48.	(56, 32)	39715·01	**2775·79**	42490·80	**2731·06**	45221·86	(52, 7)
					3279·56	45770·36	(33, 250)
49.	(41, 16)	41048·04	**2772·74**	43780·72			
	(78, 41)	41007·98	**2732·68**				

Very many of these lines occur in high wave numbers, and for these observation errors may amount to a unit or more in the wave number. In several cases different observers vary so much as to suggest different lines (? displaced). In Ag there seems to be a distinct clustering round 850·91 with four readings differing from this by −·23, +·23, −·04, +042, pointing to a displacement in the case of a Y_2 link. Near the calculated values we find

for $Y_1=811·24$ values 810·58, 11·50, 11·60, 10·47, 10·57, 10·3, 11·8,
$X_1=808·22$ „ 808·75, 8·23, 7·65, 7·75, 7·71,
$Y_2=846·76$ „ 847·31, 6·95, 6·86,
$X_2=843·61$ „ 843·57, 2·0, 2·67,

within their respective observational errors. So also in Au

near $Y_1=2771·83$ are 2772·15, 1·90, 2·21, 2·63, 1·82, 2·11, 2·74,
$X_1=2732·81$ „ 2732·90, 2·85, 3·20, 3·44, 2·46, 1·98, 2·64, 3·34, 3·89, 2·68,
$Y_2=3282·08$ „ 3281·41, 1·19, 1·26, 2·98, 2·90, 2·46, 2·67, 2·76, 1·17,
$Y_1=3233·29$ „ 3232·85, 4·11, 2·85, 4·12, 3·44, 4·24, 3·34.

Even if some of the separations adduced have no relation to X, Y links, the evidence from the mass of cases is in striking support of their existence. For instance, of the 62 arc lines in Au 48 show these attached links, many of them several. We have to remember that with links in general we get also simultaneous displacements in one of the two terms of the series lines with which they are associated. When we know these terms we can calculate the oun shifts and we are generally enabled definitely to settle the actual displacements. When these shifts are large, as for instance in Au or for first order terms in elements with smaller ouns, an allocation is often convincing. We can of course only apply this principle when the series line to which a chain belongs is known. In the above data in Au for example, we have cases belonging to $S_1(3)$, $S_2(3)$, $D_2(2)$, $D_{11}(3)$, $D_1'(1)$, $D_2'(1)$, $P_2(1)$, $P_1(1)$. Now in gold the oun shifts in the terms involved are:

$s1.$	$p_1 1.$	$p_2 1.$	$d_1'1.$	$d_2'1.$	$s3.$	$d2.$	$d3.$
39·9	10·77	13·90	22·74	23·18	1·723	2·914	1·228

The large shifts involved in *s* 1, *p* 1, *d* 1 are so great that the links would be distorted beyond the deviations we have allowed for in forming the above lists. The material at hand for the above series lines treated on this basis gives the following results. The displacements are supposed to have been produced in the spark lines.

$D_2'1$ one		$(\delta_1)D(\delta_1)$	gives		9·28	makes	sep.	$+3281·08=Y_2-1$	$d\lambda=$ ·26 *
$D_1'1$ one		0						$+3732·90=X_1+·09$	−·02
S_13 one		$-\delta$	on $s3$	„	−6·89	„	„	$-2771·80=Y_1-·03$	·004
S_23 six		$-\delta$	„	„	−6·89	„	„	$-3233·72=X_2-·43$	−·09
	back	δ_1	„	„	1·72	„	„	$-2772·06=Y_1+·23$	−·05
		$-\delta_1$	„	„	−1·72	„	„	$-2733·00=X_1+·19$	−·04
		$3\delta_1$	„	„	5·17	„	„	$+2732·10=X_1-·71$	* (·10)
	forward	$-\delta_1$	„	„	−1·72	„	„	$+2771·83=Y_1+0$	0
		0						$81·26=Y_2-·82$	* (·10)
$D_{22}2$ two		δ_1	„	d_2	2·914	„	„	$-3282·15=Y_2+·07$	−·02
		$-2\delta_1$	„	„	−5·83	„	„	$3281·34=Y_2-·74$	* (·12)
$D_{11}3$ three		$-\delta_1$	„	d_3	−1·23	„	„	$+2772·10=Y_1+·27$	−·04
		$2\delta_1$	„	„	2·45	„	„	$+3282·08=Y_2+0$	0
		δ_1	„	„	1·23	„	„	$+3233·22=X_2-·07$	·01
P_21 two		0						$-3236·78=X_2+3·49$	† −·4
		0						$+2765·64=Y_1-6·19$	† +·4
P_11 one		0						$+3282·76=Y_2+·68$	−·03

With the exception of those marked with * † all the new values are within observation errors, and the agreement is convincing as they occur with such large oun shifts and with displacements on a single term (the first excepted). The lines marked * may be false links or, since their deviations are the same (·8), this may be due to some double displacement, *e.g.* (1) S_23 (7) gives −·84 and (1) D_22 (5) gives ·67. The † suggest also the entrance of double displacements, *e.g.* (2) P_21 (6) shifts 3·6.

We shall now in discussing the maps consider the existence of Δ links based on the *d* (1) terms as established and that Rydberg's 212 separations comprise the links in question. The extraordinary importance of this fundamental quantity Δ in the constitution of spectra is thus further emphasized.

8. We are now in a position to discuss the satelloid data for link modification, taking the various maps in succession.

Map I. (2, 5, 8, 6) involving ($7x$, $10y$, $12x$, $9x$) * of Table I. The satelloid of (2) occupies the exact $u-e$ from P_1 and a Rydberg's u is continued on from it. Then a new chain starts from the main line to (4) and passes to the first satelloid of (5) on to that of (8) and continues to (10). Again new chains start from the main lines of (5, 8) and other modified ones start from the satelloids of (6). That from the red satelloid of (6) and the $+u$ to (13) form a parallel inequality since $1000{\cdot}06-681{\cdot}02=e-u+{\cdot}13$.

Map II. This is an extension of I involving the X, L, M separations. It contains three additional satelloids (3, 17, 30) or ($8y$, $11x$, $15x$) of Table I. Note the series inequalities from each satelloid of (3), viz. $682{\cdot}00+679{\cdot}36=2u+{\cdot}10$ and $693{\cdot}05+691{\cdot}41=2v+{\cdot}30$. When three lines show a series inequality it means that the extreme lines suffer the same displacement, so that here the satelloids represent the normal positions. A normal L separation links the second violet of (5 I) to the extreme red of (17), whilst a true u passes from the main of (17). From the satelloid of (8 I) is a series inequality $208{\cdot}54+211{\cdot}11=2X_1-{\cdot}03$. (30) is an x satelloid—sep. $5x$—and the modified e links suggest an unobserved satelloid at $-y$ of the one seen, making exact e.

Map III. contains sets parallel to those of (8, 10) of I, and is noticeable for the number of X links. (3, 4, 5, 10, 13*a*) are the satelloids ($16y$, $13y$, $14x$, $18y$, $17x$) of Table I. Note the true u to the extreme satelloid of (3). Indeed, if (1) is ·08 ($d\lambda={\cdot}008$) too large, the two successive links become exact, viz. $X_2=212{\cdot}26$ and $u=680{\cdot}63$. Also, while we get X_1 between the mains of (4, 5) we also find it between two of their satelloids. In (4) the modified u requires an unobserved satelloid at $-2y$ (the violet is $5y$). In (5) the first satelloid gives a normal M forward, the second has X_1 back and a modified v which indicates a third satelloid displaced a further x. So in (10) the links are definitely attached to the satelloids, but are modified indicating unobserved ones, as the u, e form a series inequality since $679{\cdot}95+1000{\cdot}62=u+e+{\cdot}16$; whilst the 209·26 becomes an exact X_1 if there be an additional violet, y further out. In (13*a*) we get a remarkable example of the satelloid representing the true linked line with the formula $P_1(b+1).3u.v+0$.

Map VI. In the P(1) portion (16, 47, 51) are ($5y$, $6y$, $4y$) of Table I. In (16) the links e, L. belong definitely to the first violet satelloid. At (47), again, the composite link $u+v$ goes to the first violet satelloid. In (51) the main only is involved.

* The x, y refer to the x, y nature of the sets in Table I.

Map VIII. In this occur (5, 7) or ($1y$, $2y$) of Table I. The map was drawn from S(3), but these sets are excluded by false links. (5) shows no links, but (7) is noticeable for a pair of parallel links from its extreme satelloids. It will be recognized that the statement at the end of § 3 is fully justified.

The 130, 50 *separations.*

9. Returning now to the consideration of the L, M separations, a glance at the maps will show that they occur in those depending on P(1), S, D, D_1' links, of which the only common term is $p(1)$. On the contrary, they do not appear connected with the following, which do not contain the $p(1)$ term. The data are in wave number.

P(2) or region.				
36172	$d_2'-p(2)$	21503	F(3)	All Shenstone's sets except his p_c, p_d
104		532		
20646	$d'-d(1)$	23929	$F_1(4)$	$d_2'-p_e$
543		25328	F(5)	$Y-p_h$
574		27338	Q_1	$d_2'-p_h$
21494	$d_2 1-d(3)$	584		
298		45821	Q_2	

Of Stücklen's two multiplets (18 lines in all) numerous X links are found attached but only one M to a very doubtful constituent of her second multiplet, the same as the Q_2 above. The origins of Shenstone's sets are not yet known, and some of them appear to be link related. His $Y-p_c$ is (13) of map III., his $d_2'-p_c$ is a satelloid, (11) of Table I. and (17) of map II. Also his p_d term is possibly merely a link connexion to p_c. His $d_2'-p_d$ is (23) of map I. All these maps belong to P(1) connexions. $d_2'-p_e$ is (16) of III., *i.e.* belongs to P(1). $Y-p_h$, $d_2'-p_h$ come in IX. and are there treated as involving $p(2)$. Also, $p_g-p_h=2e+Y_1$ and $d_2'-p_g$ is a satelloid and (3) in III. Thus the Shenstone exceptions are probably only apparent except in IX., where the two L, M may be spurious.

If, then, the L, M separations depend on displacements in some one term, that term must be the $p(1)$. We find several successions of L separations. If it is possible to transform each to some common value by displacement on the terms known to be involved in each case, it is an argument in favour of a link theory. If, on the contrary, they constantly increase or constantly decrease, we are led to suspect successive displacement as the origin. There is one such long series in map II. with 130·02, 128·91, 130·27, 128·88, 129·81; but we shall see reason to regard the 130·02, 128·91 as mere coincidences. There is another of 132·96, 132·23, 128·93, 130·98 in map IV. which show a tendency to regular decrease, especially when the 128·93 is seen to follow an enlarged *u*, i. e. a *u*-link which has encroached on it by 3·30. Very frequently the L, M occur in connexion. Also successive M's are frequently met with. In map VI. this is very noticeable. Here not only is the Rydberg set repeated by the *u*-link but we get similar repetitions by the *e*, and we find the increasing values 129·71, 130·10, 52·04, 53·79. Another increasing set is in map V. of 47·50, 50·43, 51·84. All these examples point to shifts by successive displacements of about the same amount. We shall test the data on this basis.

To produce shifts of about these amounts the displacements must be near $a=26\delta=104$ ouns and $b=10\delta=40$ ouns. These produce the following shifts:—

$+a$	on p_1 = 128·05	on p_2 = 129·56
$-a$	„ = 128·84	„ = 130·39
$+b$	„ = 49·31	„ = 49·89
$-b$	„ = 49·47	„ = 50·05

Provisionally we shall use these *a*, *b* as near the normal displacements. The testing is rather tedious as each case has to be specially calculated. The procedure is, however, rendered easier by first calculating the values of the displaced p_1, p_2 for successive *b* and *a* together with the shifts per oun for each value. For instance, if say, $(-3a+b-1)p_1$ is required, $-3a+b-1=-68\frac{1}{4}\delta=-7b+7$. The value required is given by the table for $-7b$ and the change per oun. Thus the new value of the p_1 is $31873{\cdot}21-7\times1{\cdot}2554=31864{\cdot}42$. The table is given as an Appendix. Since $\Delta=50\delta$, $(-xb)p_1=(5b-xb)p_2$. Also it should be remembered that the shift in a term is in the opposite direction to the displacement, so that for instance a positive displacement entered on the left of the series line symbol diminishes the wave number, whilst if on the right it increases it. Thus $P_1 1(-)$ is a diminished wave-number whilst $(-)S_1 m$ is increased, although the displacement on p_1 is the same in both. It will be sufficient here to discuss in some detail a few important illustrative cases only. A more complete discussion is given in the notes to the maps, although, as the general laws of link connexion are now well established, all the lines of all the maps are not dealt with.

We begin with a portion of map IV., containing lines based on the $S_1(2)$, $S_2(2)$ series lines. The majority of the wave-lengths have been carefully measured by one observer, who has given estimates of his probable errors (·01 to ·05 Å.U.); also with the small wave numbers involved the ratio $dn/d\lambda$ is small. Further, the map itself is a reliable one for the ordinary known links. The Cu spectrum is noticeable for the large number of separations close to that of the series doublet (248·44). A few have been included in this map, although there are others. The lines in the region measured by Meggers are well spread out, but there are a few regions of smaller wave-length, where the lines come close together, and in many cases are seen to depend on displacements of a few ouns. Some of these are indicated in the map by one or two additional circles. In all cases the usual displacements concurrent with links depend on a few ouns only, so that the shift per oun on $s\,2$ may be taken as constant, those on the p will of course vary largely and are given in the Table A in the Appendix. Its value for $s\,2$ is ·5856. The linkage in general is supported by the large number of similar and parallel links. It is noticeable also for the back L-separation and for the long double links $e+u$ from both S_1 and S_2 without representatives for e or u alone. That from S_1 is in defect by 1·89 accounted for by $(+\delta_1)S_1(-\delta_1)$, which shifts $1{\cdot}235+{\cdot}585=1{\cdot}82$ with $dn={\cdot}07$ (prob. O, $E={\cdot}1$). The other from S_2 is ·48 in defect accounted for by $(-\delta_1)S_2(-3\delta_1)$. We shall consider specially here for our immediate purpose of discussion of the origin of the L, M, the long chain from S_2 round by (2, 3, ... to 10). First we notice the corresponding 130·23 back from S_1 and 132·96 from S_2. Now, $(a+2$[*]$)S_1$ produces a shift 130·50, i.e. $dn={\cdot}27$ and is too large. But $(a-2)S_1(-8)$ has $dn={\cdot}05$. Similarly the back link from S_2 is met by the same $a-2$ and is $(a-2)S_2(-10)+{\cdot}03$. In the S_1 the long linked line to (4) is $(1)S_1(-1).e.u+{\cdot}07$, and the corresponding one from S_2 is $(-1)S_2(-3).e.u+0$. The S_2 chain we are to consider has the constitution—starting from (1)—$L+(e+u)+L+u+L+u$ and then returns by $-M-u-u+L$ to (11). We note also the corresponding successive L, M at (5) and at (7).

---

[*] Here and in the sequel in denoting displacements we shall omit δ_1, and a number will denote number of ouns.

(3) is 132·23 ahead of 2, produced exactly by $(-a-1)\,|\,(1)$, so that the line is $(-a-2)\,S_2(-2)e\,.\,u+0$.

(4) is $u+3{\cdot}30$ ahead, i. e. u with concomitant displacement $(-4)\,|\,(-3)+{\cdot}03$, the line is therefore $(-a-6)\,S_2(-5)\,.\,e\,.\,2u+{\cdot}03$.

(5) is 128·94 ahead. This is L modified by the foregoing displacement. The formula is $(-2a)\,S_2(4)e\,.\,2u+{\cdot}06$, or the L appears as a normal additional on $(-a)\,S_2(4)$.

(6) is $u-1{\cdot}29$ ahead and is $(-2a+1)\,S_2(4)e\,.\,3u+{\cdot}03$, the oun displacement giving 1·265.

(7) is 130·98 ahead and is $(-3a-1)\,S_2(-2)e\,.\,3u+{\cdot}01$.

(8) is 50·21 (*i.e.* M) behind. It is $(-3a+b-2)\,S_2(-3)\,.\,e\,.\,3u+0$, the M being produced by $(b-1)\,|\,(-1)$.

(9) is $u-{\cdot}02$ behind and is $(-3a+b-2)\,S_2(-3)\,.\,e\,.\,2u+{\cdot}02$.

(10) is $u+{\cdot}13$ behind and is $(-3a+b-1)\,S_2(-1)\,e\,.\,u+0$.

(11) is 129·10 ahead and is $(-4a+b-2)\,S_2(-9)\,.\,e\,.\,u+{\cdot}01$.

(16) is 51·64 ahead of (7) and is $(-3a-b-2)\,S_2(-2)\,e\,.\,3u+{\cdot}01$.

We have now a cycle round from (3) to (10), separated by 211·61. If this represents some modified X-link, then one of the L or M in the chain must be false. If it is not, then (3), (10) are simply mutually displaced, viz. comparing their formulæ above by $(-2a+b+1)\,|\,(1)$. This, as we have seen, gives exact 211·61. Again, the L sep. 129·10 to (11) must have a different signification according to the two suppositions, viz. displacement on $(-a)\,S_2$ if 211 is a link, and on $(-3a+6)\,S_2$ if it is merely a displacement and the chain is real. We should therefore be able to use these two facts to get a decision.

A. If 211·61 is a link it is one of $X_1+1{\cdot}73$, $X_2-{\cdot}66$, $Y_1+1{\cdot}40$, $Y_2-{\cdot}93$. The displacement per oun on $(-a)p_2$ is 1·257, and I see no simple arrangement to meet the deviations except $(1)\,|\,(1)=1{\cdot}257-{\cdot}585={\cdot}67$, which is good in itself for $X_2-{\cdot}66$, but with so many choices we might expect at least one coincidence. Again, on this supposition 129·11 depends on $(-a)$ on $(-a)p_2$ giving 131·18 with 1·265 per oun on the p_2. The 129·11 is therefore $(-2a)p_2-(-a)p_2-2{\cdot}07$. I can see no way to get near the 2·07 by multiples of p and s shifts. This therefore speaks strongly against the X-link supposition for 211.

B. Here, as we have seen, the shift 211·61 is exactly given by the displacement theory, and at the same time 129 falls in naturally as an L separation with error $dn = {\cdot}01$ or $d\lambda = {\cdot}005$. We thus get striking support for the reality of the chain here discussed and the suggested origin of the L.

We have here a remarkable regularity in alternation of link and displacement. To show this we reproduce the values found above, starting from (1) which is really $(a-2)S_2$:

$$(a-2)\,|\,(-10)\text{——link——}(-a-2)\,|\,(-2)\text{——link——}$$
$$(-2a)\,|\,(4)\text{——link——}(-3a-1)\,|\,(-2)\text{——}.$$

A similar system of alternating links and displacements exists in the Au $S_1(3)$ [*] linkage, the links involved being the $a=3195$ [†] and the successive displacements by Δ, Δ being the large number 113961. As in the present case this also starts by a backward displacement Δ, and the chain runs from $+\Delta$ to -3Δ. If X denote the line 23966 in $\mathrm{Au} = S_1(3) + a(2)$, we may write the set:

$$(\Delta)X,\quad X,\quad X-a(2),\quad (-\Delta)X-a(2),\quad (-\Delta)X-2a,$$
$$(-2\Delta)X-2a,\quad (-2\Delta)X-2a-a(4),\quad (-3\Delta)X-3a,$$
$$(-3\Delta)X-4a(1).$$

i. e., alternate displacements by $-\Delta$ and alternate link deductions $= a$. The parallelism is very striking. The values of the lines discussed above may be tested by direct calculation [‡].

---

[*] Trans. Roy. Soc. 217. p. 382 (1916).

[†] The a link, not the $a = 26\delta$ of the present paper.

[‡] *E. g.* take $(10) = (-3a+b-1)S_2(-1)\,e\,.\,u.$ Here $-3a+b-1 = -68\delta-\delta_1 = -7b+7\delta_1$. The table in the Appendix shows that $-7b$ increases the limit by 352·82 and the oun shift is 1·270. Hence

$$\begin{array}{lrr}
-7b & \text{increases} & 352{\cdot}82 \\
+7\delta_1 & \text{decreases} & 8{\cdot}89 = 7\times 1{\cdot}270 \\
\hline
 & & 343{\cdot}93 \\
-\delta_1 \text{ on } s & \text{decreases} & {\cdot}58 \\
\hline
 & & 343{\cdot}35 \\
 & S_2(2) = & 12601{\cdot}80 \\
 & e = & 999{\cdot}80 \\
 & u = & 680{\cdot}63 \\
\hline
 & & 14625{\cdot}58
\end{array}$$

which is exactly the value observed.

Taking the L, M displacements as following one another in the chain, they are successively $-a+2$, $-a-2$, $-a+2$, $-a-1$, $b-1$, $-b$, $-a$. If the L, M depend on definite, the same displacements, with small concomitant ones, the values indicated by this map are a, b. In fact the deviations shown come in by the necessity of making the formulæ fit within O.E. If slightly larger O.E. be admitted the formulæ in question may be written, dropping the link signs:

$$(a)S_2(-6)+{\cdot}15\ ;\quad S_2\ ;\quad (-a)S(2)+{\cdot}12\ ;\quad (-2a)S(4)+{\cdot}06\ ;$$
$$(-3a)S+{\cdot}11\ ;\quad (-3a+b)S(1)+{\cdot}20\ ;\quad (-3a-b)S(2)+{\cdot}21\ ;$$
$$(-4a)S(-5)+{\cdot}21.$$

The 5th, 6th, 7th depend on Aretz and may be allowed, but Meggers definitely excludes the 1st, 3rd, and last.

We take our next illustration from map VI. This map is remarkable for the number of exactly equal separations and of parallel repetitions of sets produced by e, u, and X links —the v here playing a very subordinate part. It was first drawn as starting from $S_1(5)$, with which it is connected through the large 214·86 link, only introduced because in arranging the raw material wide limits were admitted in searching for the X separation, with at that time uncertain values. Also $D_{11}(4)$, a very weak and unstable line only observed by Hasbach, is 208·32 from (12), or the more accurate $D_{12}=D_{22}-v$ distant 210·64. Neither of these separations is near the calculated values nor the maxima of the occurrency curves, and it would appear *à priori* extremely unlikely that such a definite and well-marked linkage should be associated with these weak lines. But the lines at (24) (25) appear in the P(1) map, thus indicating association with the P(1) lines. Moreover, the map contains some of the satelloid lines, and as the connexion of P(1) with other satelloids is quite definite this is an additional indication that the map is based on the P system. The line at (24) is (12) in map I. with the value $2e\,.\,u\,.\,P_1(-1)\,.\,v-3y+0$. No. (1) of the present map lies on a complete cycle through (24) and thus has two chains to it, viz. (L, M, X now representing link types),

$$-L+X+e+L^{*} \qquad = e+X,$$
$$-X+M+e-M+X+X = e+X.$$

---

[*] A series inequality, since $1000{\cdot}95+127{\cdot}36=e+128{\cdot}51$ with a normal L and the 1·15 on e is $2y+{\cdot}01$.

Hence (1) is (24) $-(e+X)$ links $+$small displacements, and *does not involve* the L, M separations themselves. Thus the link connexion of (1) is (taking X_2) $= X_2 . 3e . u . P_1 . v = 27583\cdot38$ by calculation, while (1) itself is 27584·18 or $X_2 . 3e . u . P_1 . v + \cdot80 = Y_2 . 3e . u . P_1 . v + 1\cdot07 = Y_2 . 3e . u . P_1 . v + 2y - \cdot07$ or $2x - \cdot01$. The important point is that (1) depends on $P_1(1)$ with a possible one or two ouns displacement. For our purpose of testing the displacement theory as the origin of the L, M separations the attached links do not affect the discussion. We may write (1) as $X_2 . P_1 + Z$ where Z is a number, and the L, M values will depend only on P_1. In other words, if we discuss the various lines connected with (1) treated as $X_2 . P_1$, their real values are those thus deduced $+Z$. To indicate this we shall write Q for $P_1 + Z$, so that the actual line at (1) is $X_2 . Q$. Starting from (1) there are the set (1, 2, 3, 4, and 49) with the separations 132·22, 50·36, 129·71, and 42·23, the last only introduced because of its $-u$, $+X_2$ links, parallel to those of the others. The formulæ (see notes to map) show that the first set depend on $-a$, $-b$, $-a$ displacements in p, with concomitants in other terms. The 42·23 of (49) may be M greatly distorted by other displacements. The arrangement shown in the tables makes its p-displacement $= -b-2$, but it has no weight for the present discussion. With these four lines we get a set of four linked by $-u+y$, and another set by $+X_2$, involving the same a, b, a, b displacements but of course not serving as additional evidence. We get, however, an independent set of four linked to (3) by $-X_2$ with separations 130·10, 52·04, 53·79. Again, the formulæ show that they depend on successive p displacements of a, b, b. From these and (3, 8) we get corresponding lines linked by e. There is another L, M set in this map between (26, 27, 28) of 128·93, 50·40 again produced by a, b. Lastly, there are parallel isolated sets 124·91 and 133·07 from (31, 32). If R stands for $3e . X_2 P_1(-a-b-2) . 2u . v - 3y + \cdot10$, (34) is $R + 125\cdot01$ and (33) is $Y_2 . R + 133\cdot21$. Now $+a$ on R shifts 129·15, so that these lines are $R(a) - 4\cdot14$ and $Y_2 . R(a) + 4\cdot06$. These are within O.E. ($dn = \pm\cdot1$) of being equally and oppositely displaced in some independent way met by $7y$—in other words, they are L lines dependent on a. This map therefore affords strong support for the present theory. The argument is strong because the lines are very accurately measured and the oun shifts at disposal are large, 3·43, and 1·24, but it is weakened in some instances by the small but definite displacement unit, $y = \cdot57$.

Still dealing with P relations we may take map II., which comprises X, L, M separations dependent on the lines of map I. The notes to this map are well worth studying for the ordinary link effects. Here we confine attention to the L, M separations. Referring to the map and notes, we see at once that several false L, M are present. Thus, 130·02, 51·90 from P_1, P_2 to linked lines are excluded. For the same reason, of the two from (13), 128·91 + 130·27, at least one must be a false L and there must at least be one false in the cycle (17, 18, 19, 8I to 5I). The 53·15 of (2) from P_2 looks excessive, but so also does the succeeding $130·94+3·58=134·52$ to (3). The two together, however, form a more normal L—M and give the formula $P_2(-a+b-1)+·03$ for (3), whilst (2) becomes $P_2(b+2)-3y-·01$. Again, the 50·04 to (8) is produced by a displacement of b alone. (10) is displaced an exact 3 ouns from (9), and the 50·04 is again given by b. All this set strongly support the a, b displacement theory. The separation of 50·30 from 4I *may* be false, although the formula is within O.E. and gives $-b$. The formula for (13) requires $-a$ and clearly shows that of the two L on either side it is 128·91 which must be excluded, whilst the two 128·88 and 129·81 fall in with great exactness but require $a-1$ and $a+2$. Again, (17, 18) fall in very closely on the supposition that 129·54 is real, and the defective formulæ for 129·80 based on this and for 50·25 based on 8I support the former by excluding these. There are a whole set from (21).

The formula for (21) is $X_1.e.(-2)P_1(a+b).2u.v-y-·06$. On this

$-(a+4)$ gives $-132·94$, *i. e.* the observed separation to (29).

$-b$ gives $-49·15$ and (22) becomes

$X_1.e.(-2)P_1(a-b+6).2u.v+·24$ within O.E. of this line.

(23) is ... $-50·60$ and $-(b+1)$ on $a-b+6$ gives 50·51

$$=X_1.e.(-2)P_1(a-2b+5).2u.v-·09.$$

(24) is ... $-130·55$, $-(a+1)$ on $a-2b+5$ gives $-129·80$ and the formula may be written

$$X_1.e.(-2)P_1(-2b+4).2u.v+y-·08.$$

The displacements for 132, 48, and 50 fall in quite naturally, but the last is artificial and the 130 may not be a real L.

Lastly, map V., depending on the inverse D set, contains a large amount of material dealing with the X, L, M separations. The oun displacements are large—2·39 for d' and

1·23 for p_1, so that conclusions as to displaced lines may be trusted. On the other hand, a large number are spark lines and the possible O.E. are larger than in some of the other maps. The map, as drawn from the observed material, shows very many false cycles indicating that there must be a number of spurious links present. The discussion of the displacements (see notes to map) definitely excludes many apparent links, and in the end it is found that all the false cycles have disappeared with the exception of the two e, u links to (10), either of which are met by possible displacements though one at least must be spurious. The 998·66 is repeated again between (13, 18), so that the 690·48 may be the spurious. The reader should follow carefully through the notes to this map.

The foregoing discussion is sufficient to show that if the M, L depend on displacements on the p term those displacements are respectively $b=10\delta$ and $a=26\delta$. The displacement for the doublet separation 248·44 is 50δ. These numbers are respectively 3^2+1, 5^2+1, 7^2+1. When we remember that the corresponding values for the doublets in Ag and Au are* 8^2+2 and 9^2 we cannot but realize that some essential relation is here indicated.

Summary.

The paper has for its main object the determination of the origins and nature of the separations in the copper spectrum in the neighbourhood of 680, 212, 130, 50, pointed out by Rydberg many years ago. The 680 is the ordinary u-link, but the other three extremely well-marked occurrences have hitherto remained unrelated. The result is to show:

(1) That the 212 are links formed by Δ on the $d(1)$ term in the same way as those already recognized are formed on the p and s terms, thus further accentuating the great part which the quantity Δ takes in the general constitution of spectra.

(2) The 50, 130 seem to be of a quite different nature and to be due to successive displacements of 10δ, 26δ in p terms, that producing the doublet separation of 248·44 being 50δ.

(3) Incidentally the properties of Hasbach's remarkable satellite systems had to be considered. It is shown that they are all related to the P(1) series lines, obey very closely displacement rules, and that they afford direct experimental evidence for the rules of link modification.

---

* 'Analysis,' p. 132. The values for Na, K, Rb, Cs also are 6^2+3, 7^2+4, 7^2, 7^2+2.

The Maps.

The maps contain the raw material for discussion. It is to be expected that a number of the separations given will not correspond to real links or L, M values, but will merely be numerical coincidences, and indeed the discussion shows that such are present and can be excluded as false or pseudo links. Such are included in [ ]. Doubtless some still remain but the proportion is probably small, for if there were a considerable proportion, the chains from one map should be expected to run on into another depending on a different series line. It is very remarkable that no such case occurs. In the maps a circle represents a line with an included number referring to an accompanying list giving the wave-lengths and wave-numbers. The small numbers outside a circle give the separations from the next lines on either side, so as to indicate the degree of crowding or the reverse in the spectrum. The important numbers for our present purpose are the separations in a chain, and these are given in block figures in the junction line between two circles. The wave-numbers increase in a chain from left to right, and when a link is drawn vertically the increase is downwards, unless an arrow is drawn in the opposite direction. The lists contain also the formulæ determined for a large number of the lines involved, especially where the L, M occur. These indicate the displacements required and also give the wave-number difference from the observed value, which should be less than the probable observation error. Unless this condition can be met without involving more than a few ouns displacement on the two terms entering, the link is regarded as a false one. Lines observed in R.A. are entered in italics. They are mostly spark lines by E.V.

Map I. P(1).

$P_2(1)=3273{\cdot}967,\ 30535{\cdot}217\,;\ P_1(1)=3247{\cdot}550,\ 30783{\cdot}59.$

Oun shift on $s(1)=3{\cdot}43$.

The map contains the linkage from P(1) involving e, u, v.

1	2	3384·815	29535·26	$e\,.\,P_2-{\cdot}16$	$=e\,.\,P_2(-1)+2y-{\cdot}05$
2		8·55	16·06	$e\,.\,P_2\,.\,u+{\cdot}01$	} is sat. (7)
	8	3307·952	30221·51	...... $+10x+{\cdot}06$	
3	4	3235·712	30896·21	$e\,.\,P_2\,.\,2u-y+{\cdot}10$	
4	2	3233·89	30913·62	$e\,.\,P_2\,.\,u\,.\,v+10x+{\cdot}09$	

P(1) (*continued*).

5	4	3208·236[1]	31160·80	$e\,.\,P_1\,.\,u\,.\,v+10x-2y-{\cdot}02$	is sat. (10)
		8·119	61·93	.... $-{\cdot}03$	
		7·94	63·69	.... $+3y+{\cdot}02$	
		7·65	66·50	.... $+10y-{\cdot}02$	
6		80·687	72·67	.... $-5x-y+{\cdot}06$	is sat. (9)
		80·40	75·34	.... $-y+{\cdot}03$	
	3	3279·823	30480·69	$e\,.\,P_1\,.\,v+10x-y-{\cdot}02$	
		9·54	83·33	.... $+15x-y-{\cdot}08$	
		9·06	87·78	.... $+23x-y+{\cdot}05$	
7	3*n*	3175·73	31479·75	$P_1\,.\,v+10x-2y-{\cdot}19$	
8	6*n*	3108·603[2]	32159·49	$(-2)P_1(-3)\,.\,u\,.\,v+0$	is sat. (12)
		8·43	61·55	$(-2)P_1(-3)\,.\,u\,.\,v+4x-{\cdot}10$	
9	2*n*	3014·84	33159·64	$(-1)P_1\,.\,e\,.\,u\,.\,v+{\cdot}10$	
10	2	3044·032	32841·64	$(-1)P_1(1)\,.\,2e\,.\,u\,.\,v+{\cdot}06$	
11	1*n*	3392·01	29472·61	$2e\,.\,(1)P_1\,.\,v-{\cdot}03$	
12	3	3572·136	28792·50	$2e\,.\,u\,.\,P_1(-1)\,.\,v-3y-0$	
13	3	3315·399	30153·63	$2e\,.\,P_1(-3)\,.\,u\,.\,v+y+{\cdot}07$	
14	2*n*	3354·475	29802·40	$e\,.\,u\,.\,(-1)P_1(-3)\,.\,v+0$	

In the P maps the satelloids introduce the unknown x, y shifts and in general they have been left in the lines linked to them.

---

[1] The first satelloid is 248·31 ahead of (4) or 248·40 of its formula, whilst the P_2, P_1 are separated by 248·37, so that we get here a change from P_2 to P_1.

[2] The map shows it is a $P_1.u.v$ line and direct calculation gives the displacements indicated in the formula.

Map II.

Annex to I. with X, L, M separations. For extensions from (12, 13) of I. see map VI.

1 is (6) of I and related to P_2. Hence 51·90 is a false M.

2	3	3268·278	30588·36	$P_2(b+2)-1{\cdot}72=P_2(b+2)-3y-{\cdot}01$	

53·13 is excessive, but it is followed by an excessive −134·52 to (3) giving a more normal L–M. Moreover, the formula gives the value very exactly. We must suspect that (2) has a satelloid $3y$ less.

3		3·09	50·36	$(-1)P_2(\qquad)-{\cdot}02$	is sat. (8)
	4	3282·716	30453·84	$P_2(-a+b-1)+{\cdot}03$	
		2·33	57·42	$(+1)P_2(\qquad)+{\cdot}18$	

This satelloid set does not depend on y, but the seps. are due to ± one oun displacement in $s(1)$. We note the symmetrical series inequalities in u from one and v from the other satelloid.

4	1	3358·76	29764·37	$v.(-1)P_2(-a+b-2)+y-{\cdot}12$
5	1*n*	3209·47	31148·83	$(-1)P_2(-a+b-2)+y+{\cdot}18$
6	1	3358·31	29768·36	$u.(1)P_2(-a+b-2)-{\cdot}14$
7	2*nb*	3211·44	31129·72	$(1)P_2(-a+b-2).u-{\cdot}04$
8	2	3277·331	30503·88	$P_2(-a+2b-1)-{\cdot}05$
9	1*n*	3223·044	31017·64	$(-1)P_2(-2a+b-2).v+y-{\cdot}15$
10	3*n*	3223·24	31014·00	$(-1)P_2(-2a+b-2).v+y-3{\cdot}79$

i.e. is (9) displaced by 3 ouns $=(-1)P_2(-2a+b-5).v+y-{\cdot}01$

11	1*n*	3218·23	31064·04	$(-1)P_2(-2a+2b-5).v+{\cdot}15$

A separation of 130·02 is shown as between $P_1(1)$ and (4) of I, linked to it. Hence 130·02 is a false L.

12	1*n*	3239·16	30863·32	$e.P_2(-b)u.v+9y+{\cdot}11$

is 50·30 behind (4) of I $=e.P_2.u.v+10y-{\cdot}21$

13	3*n*	3293·903	30350·42	$e(-1)P_1(-a)v-{\cdot}05$

This divides the separation between the linked (2) and (6) of I. Of the two L links represented, one at least is therefore false. Regarded as dependent on (6) of I, the formula reproduces the line exactly; if it depends on 2 of I (+128·91), the formula is $e(-1)P_2(a+1)+{\cdot}11$ outside O.E. This decides in favour of 130·27 being real.

14	4	3317·225	30137·04	$X_2.e.P_1(-a)v-2y-{\cdot}02$
15	3	3266·814	30609·57	$e.(-2)P_1(a-1).v+0$
16	2	3252·22	30739·38	$e.(-2)P_1(2a+1).v+{\cdot}13$
17		4·66	3·23	$e.(-2)P_1(a+1).u.v+y+0$
		4·34	6·36	.... $(a+5)$......$-2y-{\cdot}03$
	6	3194·103	31298·67	$e(-2)P_1(a+5)u.v+2y+0$
		3·979	9·89	............$(a+6)$ ... $+2y+0$
		3·81	301·35	............$(a+7)$ ... $+2y+{\cdot}23$

is sat. (11)

We come here to a false cycle, with at least one false L or M. Either the 129·54 is real, connecting (17) to (5) of I whose satelloid in question is $e.P_1.u.v+10x+3y+{\cdot}02$ $=e.P_1.u.v+7{\cdot}13$. In this case one at least of the L, M 129·80, 50·25 must be false, or the latter may be real and 129·54 false, or both sets false. On the first supposition the longest satelloid of (17) is $e.P_1.u.v+7{\cdot}13+129{\cdot}54$. Here $a+1$ on p_1 shifts 129·27 and we get $e.P_1(a+1).u.v+7{\cdot}43$ $=e.(-2)P_1(a+1)u.v+y+0$. The main line is 5·44 larger, which is $4\delta_1$ on $p_1(a+1)+y+0$. This explains the failure of the y-multiple for the extreme satelloid in Table I. of the satelloids. Also the first violet 1·22 with very exact measures is δ_1 on $p_1(a)$. The formula for the main is therefore as entered above. Not only therefore do we get exact formulæ with this separation as a real L, but the current term $p_1(a)$ entering enables us to explain the satelloid separations, a difficulty in discussing Table I.

18 6 3126·106 31979·44 $e\,.\,(-2)P_1(a+5)2u\,.\,v+2y+{\cdot}14$
$=e(-2)P_1(a+6)\,.\,2u\,.\,v+{\cdot}03$

19 2 3113·468 32109·24 $e\,.\,(-2)P_1(2a+8)\,.\,2u\,.\,v+{\cdot}22$
or $(-2)P_1(-b-3)\,.\,u\,.\,v-{\cdot}78$

This may be either 129·80 on (18) *or* −50·25 on (8) of I, which is $(-2)P_1(-3)\,.\,u\,.\,v+0$. The resulting formulæ would be as entered. As $\cdot 78=y+{\cdot}21$ both are equally probable or improbable according to the simplicity with which ·21 can be met. $p_1(3)-6y$ gives −·02 in the first and $p_1(-2)+4y$ gives −·02 in second—both artificial—contrasted with exact reproduction of the sep. 129·54 at (17). We cannot in this kind of reasoning, especially with the presence of y, get certainty, but the 129·80 and 50·25 are marked as false. This is sustained below under (31, 32).

20	1	3118·355	32058·91	27	2	3149·501	31741·90	
21	4*n*	3146·821	31768·94	29	2	3160·047	31635·98	
22	1*n*	3151·61	31720·66	30	6	3063·416	32633·84	} sat. (15)
23	3	3156·623	31670·30			3·18	36·35	
24	4*n*	3169·680	31539·84	31	4	3128·692	31953·01	
25	3	3088·121	32372·79	32	2	3149·501	31741·90	
26	4	3128·692	31953·01					

Nos. (21...24) and (29) serve for evidence on the L, M origins. (21) is $X_1\,.\,e\,.\,(-2)P_1(a+6)\,.\,2u\,.\,v-y-{\cdot}01$. A displacement $-(a+4)$ on $p_1(a+6)$ shifts 132·94, the observed 132·96 to $(29)=X_1\,.\,e\,.\,P_1(7)\,.\,2u\,.\,v+{\cdot}12$; $-b$ on $p_1(a+6)$ shifts 49·15, so that (22) becomes $X_1\,.\,e(-2)P_1(a-b+6)2u\,.\,v+{\cdot}24=X_2\,.\,e\,.\,(-2)P_1(a-b+6)\,.\,2u\,.\,v-{\cdot}03$; $-(b+1)$ on $(a-b+6)$ shifts 50·51 and (23) becomes $X_2\,.\,e\,.(-2)P_1(a-2b+5)\,.\,2u\,.\,v+{\cdot}12$; and $-(a+1)$ on $a-2b+5$ gives 129·80 and (24) is $\ldots(-2b+4)\ldots -y+{\cdot}03$. All these support the displacement theory of L, M.

(31, 32) are the same as (27, 26), so that there is a cycle, viz. starting from (31), $u-e+L-X-u-L+e+X$ which annul, so that we get a true cycle. It is interesting to note that had we made the 129 at 17 false and included 129·8+50 between 18 and 8 I, the links would not have annulled and the cycle would have been false.

Map III.

This map starts from two parallel sets to (8) and (10) of I, indicated at the top of the map. 8 I is $(-2)P_1(-3)\,.\,u\,.\,v+0$, or if cleared of displacements is $P_1\,.\,u\,.\,v+3{\cdot}16$. Thus (1) is $P_1\,.\,u\,.\,v+93{\cdot}22$ and (4) is $P_1\,.\,u\,.\,v+155{\cdot}03$. Now $(2b-4)$ on p_1 shifts 93·62 and $3b+6$ shifts 155·06. Hence (1) is $P_1(2b-4)\,.\,u\,.\,v-{\cdot}40 = P_1(2b+5)\,.\,2u+0$, correcting the two links $-X_2\,.\,u$ to exact values. So also (4) becomes $P_1(3b+6)\,.\,u\,.\,v+{\cdot}05$.

1	4	3099·922	32249·55	$P_1(2b+5)\,.\,2u+0$	
2	2*n*	3120·452	32037·37	$X_2\,.\,P_1(2b+5)\,.\,2u+{\cdot}09$	
3	6	3036·105	32927·38	.... $-5y+{\cdot}08$	sat. (16
		6·89	29·72	.... $-y+{\cdot}11$	
		6·84	30·26	$P_1(2b+5)\,.\,3u+{\cdot}08$	
4	6	3093·993	32311·36	$P_1(3b+6)\,.\,u\,.\,v+{\cdot}05$	sat. (13)
		3·72	14·25	.... $+5y+{\cdot}04$	
5	4	3073·803	32523·58	$P_1(3b+6)\,.\,u\,.\,v\,.\,X_2+0$	sat. (14)
		3·704	24·62	.... $+2x-{\cdot}04$	
		3·53	26·35	.... $+5x+{\cdot}07$	
6	2*n*	3030·25	32991·00	$P_1(3b+5)\,.\,2u\,.\,v+{\cdot}26$	within O.E.
7	5	3010·840	33203·69	$P_1(3b+5)\,.\,2u\,.\,v\,.\,X_2-y-{\cdot}01$	
8	3	3022·608 [1]	33074·43	$P_1(-a+3b+4)\,.\,2u\,.\,v\,.\,X_1+y+{\cdot}01$	
9	3*n*	3021·56 [2]	33085·89	$P_1(-a+3b+4)\,.\,u\,.\,2v\,.\,X_1+y-{\cdot}01$	
10		1·716	54·38	$P_1(-a+3b+4)\,.\,3u\,.\,v\,.\,X_1-{\cdot}12$	sat. (18)
	6	2961·177	33760·53	$P_1(-a+3b+4)\,.\,3u\,.\,v\,.\,Y_1+10y+{\cdot}04$	
		0·92	63·48	$P_1(-a+3b+4)\,.\,3u\,.\,v\,.\,X_1+16y-{\cdot}14$	
11	1	2875·69	34764·10	$P_1(-a+3b+4)\,.\,e\,.\,3u\,.\,v\,.\,X_2+17y+{\cdot}11$	
12	2*n*	2979·38	33554·22	$P_1(-a+3b+4)\,.\,3u\,.\,v+17y-{\cdot}13$	
13	2	2998·384	33341·59	$X_2\,.\,P_1(-a+3b+4)\,.\,3u\,.\,v+16y+{\cdot}08$	
14	1*n*	2911·21	34339·95	$X_2\,.\,P_1(-a+3b+3)\,.\,e\,.\,3u\,.\,v+16y-{\cdot}13$	
15	4	3140·318	31834·72	$P_1(3b+6)\,.\,u\,.\,X_2+6y-{\cdot}02$	
16	2	3068·912	32575·37	$P_1(4b+8)\,.\,u\,.\,v\,Y_2+{\cdot}11$	
17	1*n*	2991·76 [3]	33415·42	$P_1(3b+6)\,.\,u\,.\,v\,.\,2X_2-2y+{\cdot}03$	
13*a*	4	2997·363	33352·97	$Y_2\,.\,P_1(b-1)\,.\,3u\,.\,v-{\cdot}14$	sat. (17)
		7·13 [4]	55·57	$Y_2\,.\,P_1(b+1)\,.\,3u\,.\,v+0$	
12*a*	2*n*	2978·293	33566·51	$P_1(b-1)\,.\,3u\,.\,v+{\cdot}84$	
18	1*n*	2985·88	33481·22	$X_2\,.\,P_1(a+b+1)\,.\,3u\,.\,v+y+{\cdot}06$	
19	1*n*	2982·77	33516·11	$P_1(-1)\,.\,3u\,.\,v+{\cdot}21$	

[1] $-(a+1)$ on $3b$ shifts 129·13. Note $-a+3b+4=5\delta=\frac{1}{2}b$.

[2] The separation from (8) is exact $v-u$, i. e. one of the u is replaced by v.

[3] Note the series inequality $211{\cdot}73+212{\cdot}69=2(X_2-{\cdot}06)$.

[4] The line is 13·98 from (13), and the linkage therefore $X|3u\,.\,v$. Direct calculation for the satelloid gives then the result entered. Or the main is $11{\cdot}38=v-u-{\cdot}07$ ahead of (13), *i. e.* the $3u\,.\,v$ in that is changed to $2u\,.\,2v$. The three parallel sets in this map therefore depend on $P_1(b+1)$, $P_1(2b+5)$, $P_1(3b+6)$.

Map IV. S(2).

$S_1(2)=(10)\ 8092{\cdot}74, 12353{\cdot}36; S_2(2)=(10)7933{\cdot}20, 12601{\cdot}80.$
Oun shift on $s(2)={\cdot}5856$.

Meggers' probable errors are inserted in brackets.

S_1.

1	2	8178·96	12223·13 (03)	$(a-2)\,S_1(-8)+{\cdot}05$
2	1	8216·22	12167·70 (04)	$(a+b+7)\,S_1-{\cdot}02$
3	3	7774·18[1]	12859·56 (01)	$(a+b+7)\,S_1\,.\,v-{\cdot}26$
4	1	7124·66	14031·89 (09)	$(1)S_1(-1)\,.\,e\,.\,u-{\cdot}07$
5	1	8187·90[2]	12209·78 (07)	Q
6	1	8680·08	11517·46 (06)	$v\,.\,Q-{\cdot}24$
7	2	8446·40	11836·11 (04)	$u\,.\,v\,.\,Q(-1)\,.\,e-{\cdot}19$
8	1	8273·53	12083·53 (06)	

[1] I see no way of meeting the $-{\cdot}26$, which occurs also in (6, 7). This line should possibly be excluded. The two neighbouring lines are (2)...5·41; (4)...1·98 or $n=$...57·52; ...63·20 separated from (3) by $-2{\cdot}04$ and $+3{\cdot}64$, the latter being 3 ouns on the p_1 term.

[2] This is 13·90 ahead of (1) and is doubtless a S_1 relative. Call it Q. The last separation suggests a change from p_1 to p_2. If the 247·42 is wholly this change, p_1 must enter as $p_1(2b-10)$, that of (1) being $p_1(a-2)$, a displacement of 12δ.

$S_2(2)$.

1	2	8017·78[1]	12468·84 (03)	$(a-2)\,S_2(-10)+{\cdot}03$
2	1*n*	7000·02	14281·74 (10)	$(-1)\,S_2(-3)\,.\,e\,.\,u+0$
3	2*n*	6935·80	14413·97 (06)	$(-a-2)\,S_2(-2)\,.\,e\,.\,u+0$
4	4	6621·61	15097·90 (02)	$(-a-6)\,S_2(-5)\,.\,e\,.\,2u+{\cdot}03$
5	2*n*	6565·54	15226·84 (07)	$(-2a)\,S_2(4)\,.\,e\,.\,2u+{\cdot}06$
6	2	6285·125	15906·18	$(-2a+1)\,S_2(4)\,.\,e\,.\,3u+{\cdot}03$
7	1*n*	6233·793	16037·16	$(-3a-1)\,S_2(-2)\,.\,e\,.\,3u+{\cdot}01$
8	2*n*	6253·371	15986·95	$(-3a+b-2)\,S_2(-3)\,.\,e\,.\,3u+0$
9	1	6531·437	15306·34	$(-3a+b-2)\,S_2(-3)\,.\,e\,.\,2u+{\cdot}02$
10	1	6835·46	14625·58 (10)	$(-3a+b-1)\,S_2(-1)\,.\,e\,.\,u+0$
11	2*n*	6775·64	14754·68 (06)	$(-4a+b-2)\,S_2(-9)\,.\,e\,.\,u+{\cdot}01$
12	1*n*	6890·64[2]	14507·89 (02)	$(-4a+b-3)\,S_1(-3)\,.\,e\,.\,u+0$
	2	89·92	09·96 (06)	$(-4a+b-3)\,S_1(-1)\,.\,e\,.\,u-{\cdot}09$
13	5	6599·681	15148·06	$(-a-b-4)\,S_2\,.\,e\,.\,2u+{\cdot}08$
14	2*n*	6544·51	15275·77 (09)	$(-2a-b)\,S_2(2)\,.\,e\,.\,2u+{\cdot}09$
15	1*n*	6840·99	14613·74 (02)	$v(-3a+b-2)\,S_2(-4)\,.\,e\,.\,2u+{\cdot}06$
16	1*n*	6213·785	16088·80	$(-3a-b-2)\,S_2(-2)\,.\,e\,.\,3u+{\cdot}01$

[1] Also $(a)\,S_2(-6)-{\cdot}11$, but the residual is too large.

[2] Or more probably the $-$"*a*" link $+(1)$ on $p_1=(-4a+b-1)\,S_1(-9)\,.\,e\,.\,u+{\cdot}01-$link "*a*".

S(2) (*continued*).

17	4	6119·545	16336·57
18	1	6199·195	16126·66
19	2	6296·599	15877·20
20	2	6157·577	16235·66
	1	7·371	36·21
21	2	6427·564	15553·69
22	2	6039·798	16552·26
23	1*n*	6064·686	16484·34
24	2*n*	6045·846	16535·71
	2*n*	·085	37·79
25	4	6325·450	15804·78
26		6059·446[3]	16498·60
27	1*n*	6151·576	16251·51
28	2	6274·624	15932·80
29	2	6296·599	15877·20
	2	4·004	83·75
30	4	6243·125	16013·19
31	3*n*	6223·655	16063·28
32	2	5966·594	16755·34
33	0	6504·051	15371·02
34	1	6415·155	15583·78
35	3*n*	6146·834	16264·04
	3*n*	8·190	0·46
	4*rv*	7·310	2·73
36	2*n*	6127·729	16314·75
37	2*n*	6583·542	15185·20
38	2	6032·326[4]	16572·77
39	3	7039·34	14201·98 (04)
40	5*n*	6485·142	15415·61
41	5	6090·226	16415·21
42	2*n*	6506·142	15365·85
43	2	6230·734	16045·03
44	3	6251·316	15992·21
45	1	6150·135	16255·31
46	1	6452·287	15494·11
47	5*n*	6474·176	15441·72
48	2*n*	1·240	90·99
	2*n*	6060·860	16494·75
		59·449[3]	98·60
49	2*b*	6749·29	14812·28 (10)
50	1*n*	6404·050[5]	15610·80
	1*n*	1·427	17·21
	1	0·591	19·25
51	2	6135·585	16293·87

The lines to three decimals are by Aretz.

[3] "Heads of bands"—? analogous to satelloids.

[4] Separation taken from mean of (29).

[5] The separations are links $a-\cdot55$, $c-\cdot03$, $d-\cdot99$.

Map V. ($d'-p1$.)

$D'_{12}(1)=5700\cdot247,\ -17538\cdot24$; $D'_{11}(1)=5732\cdot364,\ -17439\cdot98$; $D'_{22}(1)=5782\cdot127,\ -17289\cdot88$.

Oun shifts on $d_2'=2\cdot3977$, on $d_1'=2\cdot3905$.

As the P lines do not enter, the x, y shifts are not admissible. The first back link from D'_{12} is $e-\cdot63$, and ·63 not being met by displacements is excluded, and the 48·12 to (2) is not therefore capable of being tested. The two lines are close parallels to two lines (24, 23) of the S(2) linkage (map IV.), and must really belong to it. There are in this map several false cycles. As an indication of connexions, we have the 248·23 between (4, 5). This doublet ν separation suggests a change between two p_1, p_2 terms. If (5) is connected to the D'_{12} through 47·51−129·63, it depends on $-p_1$ and $+\nu$ cannot change to $-p_2$. We shall start therefore in the opposite direction by the chain D_{11}, 3, 4, 5. The dashes in D′ are omitted.

1	2*n*	6045·085	16537·80	
2	1	6062·726	16489·67	false link
3	1*n*	*5663·52*	17652·53	$D_{11} . Y_2 + {\cdot}01$
4	1*n*	*5646·93*	17704·40	$D_{11}(b+2) . Y_2 + {\cdot}10$
5	1	5727·063[1]	17456·12	$D_{21}(b+2) . X_2 - {\cdot}05$
6	1*n*	*5685·03*[2]	17585·75	$D_{21}(a+b+2) . Y_2 + {\cdot}05$ (see note)
7	1*n*	5631·65	17751·85	$D_{12}(1) . X_2 + {\cdot}09$
8	3	*5679·42*	17603·12	$D_{11}(-b) . Y_2 + {\cdot}07$
9	3	*5566·35*[3]	17960·71	$D_{12} . X_1 . Y_2 + {\cdot}07$
10	1	5360·099[4]	18651·19	?
11	2*n*	*5668·77*[5]	17636·18	$D_{21}(a+2b+3) . X_2 + {\cdot}01$
12	4*n*	*5652·16*	17688·02	$(-1) D_{21}(a+3b+3) X_2 + {\cdot}09$
13	4	*5438·79*[6]	18381·97	$e . D_{11}(-b-6) . X_2 . 2Y_2 . 2u + {\cdot}06$ (see note)
14	1*n*	*5453·93*	18330·93	$(1) D_{11} . Y_2 . u + {\cdot}20$ (within O.E.)
15	0*n*	5391·629	18542·12	$(1) D_{11}(-1) . 2Y_2 . u + {\cdot}05$
16	1*n*	5200·87	19222·22	$(1) D_{11}(-1) . 2X_2 . 2u + {\cdot}06$
17	3*n*	5144·106	19434·32	$D_{11}(-3) . 3X_2 . 2u - {\cdot}03$
18	1*n*	*5158·53*	19380·62	$D_{11}(-b-7) . 3Y_2 . 2u - {\cdot}12$
19	1	*5130·97*	19484·72	$(-1) D_{11}(-b-4) . 3X_2 . 2u - {\cdot}10$
20	1*n*	*5429·01*	18414·83	$D_{11}(-a-1) . 2X_2 . u - {\cdot}23$
21	2*n*	*5408·56*	18484·70	$e . D_{11}(b-5) . 3Y_2 . 2u + {\cdot}03$
22	2*n*	5076·283	19693·98	$D_{11}(b-3) . X_1 . X_2 . 2Y_2 . 2u - {\cdot}07$
23	0	5022·770	19903·82	$D_{11}(b-3) . 2X_1 : X_2 . 2Y_2 . 2u - {\cdot}07$
24	3	*5203·74*	19212·15	$v . D_{11}(b-3) . 2X_1 . 3Y_2 . 2u + {\cdot}07$
25	2*n*	*5089·54*	19643·36	$D_{11}(-4) . X_1 . X_2 . 2Y_2 . 2u - {\cdot}13$

This map is noticeable for the alternative succession of X links, especially the $X + u + X + u + X + M + X + X$.

---

[1] The 248 suggests $-\Delta$. or p_1 to p_2. But $-\Delta$ on p_2 $(b+2)$ shifts 247·83. Note, D_{21} is a "forbidden" line.

[2] This is 129·63 ahead of (5) and 47·51 of D_{12}, one link at least being false, For the former $+a$ on $p_2(b+2)$ shifts 129·26. On this supposition the formula is as entered. Also b on p_1 shifts 49·31, and the formula based on D_{12} is $D_{12}(b-1) - {\cdot}57$ and ·57 cannot be met by any simple displacements on d_2, p_1. This points to 47·50 as being the false one. This is supported by the next 50·43 link—see note 5 below.

[3] Note the series inequality $213{\cdot}61 + 208{\cdot}86 = X_1 + Y_2 + {\cdot}02$. This and (4) are so exact that the false link in this cycle must be either 690·48 or 998·66 to (10).

[4] On the two possible suppositions of linkage to (9) or (3), the first gives $D_{12}(-1) . X_1 . X_2 . v - {\cdot}05$, and the second $(1) D_{11}(1) . Y_2 . e + {\cdot}03$. The measure is by Aretz with O.E. about ·05, so that it is not possible to decide which (if not both) is false. Both are marked doubtfully false.

[5] If based on (5) formula $= D_{21}(a+2b+3) . X_2 + {\cdot}01$, if on D_{12} is $D_{12}(2b-1) + {\cdot}63$. Thus line (11) supports (6) in making 47·50 false.

[6] The map shows three links: $v + 1{\cdot}87$ from (12) $= (-1) D_{21}(a+3b+4) . X_2 . e + {\cdot}69$, and thus excluded; 51·04 from (14) gives $(1) D_{11}(b+1) . Y_2 . u + {\cdot}70$, also excluded; whilst 998·65 from (18) gives that entered with residual ·06. The e link is thus not necessarily excluded.

Map VI. ($S_1(5)$ and $P(1)$.)

$S_1(5)$, ($2n$) 3598·01, 27785·25; $D_{11}(4)$, ($3n$) 3687·5, 27110·9.

Oun shift on $s(5)={\cdot}0504$; on $d(4)={\cdot}0646$.

$S_1(5)-{\cdot}05$[1].

1	6	3599·135[2]	27776·56	$(7)\,S_1-0$
2	4n	3512·122	28464·71	$(1)\,S_1(-1).u-{\cdot}01$
3	2	*3393·09*	29464·19	$(1)\,S_1(-1).u.e-{\cdot}33$
4	2n	*3688·60*[3]	27103·75	$u.(1)\,S_1+{\cdot}36$
		·38	05·37	$u.(-1)\,S_1-{\cdot}48$
5	2n	3695·73	27053·75	$u.(b+1)\,S_1-{\cdot}33$

---

[1] A probable correction.

[2] There is an analogous displaced line for $S_1(4)=(-7)\,S_1(4)$. The two separations are respectively $-8{\cdot}64$, $+8{\cdot}62$.

[3] The two measures are by K.R. and by Crew & Tatnall. The map takes the mean, but probably as indicated here they are ± one oun on the limit. The first (K.R.) shows the same displacement as the other lines and explains the M as a b displacement on (4).

The P portion.

(For general discussion see p. 218.)

1	2n	3624·236	27584·18	$X_2.Q$	
2	2	3641·693	27451·96	$X_2.(1)\,Q(-a)+{\cdot}05$	
3	2	3648·385	27401·60	$X_2.(1)\,Q(-a-b)-y+{\cdot}02$	
4	2	3665·740	27271·89	$Y_2.(1)\,Q(-2a-b)-y-{\cdot}05$	
5	2	3734·23	26771·70	$u.Y_2.(1)\,Q(-a)+{\cdot}11$	
6	3	3741·247	26721·49	$u.X_2.(1)\,Q(-a-b)-{\cdot}03$	
7	2	3759·495	26591·78	$u.Y_2.(1)\,Q(-a-b)-{\cdot}09$	
8	3	3613·753	27664·19	$(1)\,Q(-a)+{\cdot}01$	
9	2	3620·346	27613·83	$(1)\,Q(-a-b)-y-{\cdot}02$	
10	1	3712·000	26932·02	$u.(1)\,Q(-a-b)-y-{\cdot}20$	
11	1n	3676·37	27189·34	$2X_2.(1)\,Q(-a-b)-y+{\cdot}03$	
12	2	3659·358	27319·44	$2X_2.(1)\,Q(-b)+y-{\cdot}14$	
13	1n	3652·40	27371·48	$2Y_2.Q+{\cdot}11$	
14	2	3645·236	27425·27	$2Y_2.(-1)\,Q(b)+2y+{\cdot}02$	
15	1n	3546·45	28189·19	$2X_2.(1)\,Q(-a-b).e-y+{\cdot}08$	
16		0·67	15·18	$X_2.Y_2$ …… $(-b+1).e-8y-{\cdot}01$	sat. (5)
		0·55	16·14	…………… $(-b-1).e-{\cdot}09$	
	6	3530·388[1]	28317·44	…………… $(-b+1).e-4y-{\cdot}03$	
		0·251	18·52	$X_2.Y_2.(1)\,Q(-b).e+{\cdot}01$	
		0·10	19·75	…………… $(-b+1)\ldots+0$	
17	4	3524·240	28366·83	$X_2.Y_2.(1)\,Q.e-2y-{\cdot}04$	
18	2	3517·029	28425·00	$2Y_2.(-1)\,Q(b).e+2y-{\cdot}03$	
19	4	3520·032	28400·75	$X_2.(1)\,Q(-a-b).e-2y-{\cdot}08$	

---

[1] Compare the discussion in Table I. The true linked line is here represented by the 1st viol. sat., the 2nd is an oun shift in p on this. The main and extreme red are respectively $4y$, $8y$ from the extreme violet, and the 1st red is a two-oun shift in p from the 1st viol.

20	1*n*	3435·53[2]	29090·81	$X_2 . (1) Q(-a-b) . e . v-2y+{\cdot}07$	
21	2	3498·063[3]	28579·09	$X_2 . 2e . u . P_1(-1) . v-5y+0$	
22	1	3379·69	29580·05	$X_2 . e . u . P_1(-1) . v-3y+{\cdot}02$	
23	2*n*	3487·565	28665·14	$(1) Q(-a) . e+2y+{\cdot}02$	
24	3	3472·136	28792·50	$2e . u . P_1(-1) . v-3y+0$	
25	1*n*	3392·01	29472·61	$2e . \quad P_1(-1) . v-4y+{\cdot}05$	
26	3	3315·399	30153·63	$2e . \quad P_1(-3) . v . u+y+{\cdot}05$	
26*a*	2	3292·392	30364·34	$\ldots\ldots\ldots\ldots . Y_1+2y-{\cdot}02$	
26*b*	2*n*	3404·66	29363·11	$e . \quad P_1(-3) . u . v . Y_1+{\cdot}09$	
27	4	3329·638	30024·70	$2e . P_1(-a-3) . u . v+y-{\cdot}02$	
28	3	3335·235	29974·30	$2e . P_1(-a-b-3) . u . v+{\cdot}03$	
29	6	3450·335	28974·42	$3e\ldots\ldots\ldots\ldots -{\cdot}05$	
30	4	3475·998	28760·52	$3e . X_2\ldots\ldots\ldots\ldots -3y+{\cdot}03$	
31	2	3395·473	29442·54	$3e . X_2 . P_1(-a-b-2) . 2u . v-3y+{\cdot}10$	
32	1*n*	3420·16	29230·04	$3e . X_2 . Y_2\ldots\ldots\ldots\ldots +{\cdot}14$	
33	2*n*	3404·66[4]	29363·11	$3e . X_2 . Y_2 . P_1(-b-2) \ldots\ldots +4{\cdot}06$	
34	2*n*	3381·13[4]	29567·45	$3e . X_2 . P_1(-b-2) \quad \ldots\ldots -4{\cdot}14$	
35	1	3341·184	29920·94	$3e . X_2 . P_1(-a-b-2) . 2u . 2v-5y+{\cdot}06$	
36	4*r*	3365·353	29706·06	$3e . X_2 . Y_2\ldots\ldots\ldots\ldots -8y-{\cdot}01$	
37	1*n*	*3817·45*	26189·60	$e . 2X_2 . (1) Q(-a-b)-y+{\cdot}09$	
38	2	3720·770	26868·57	$e . 2X_2 . (2) Q(-a-b+1) . u+{\cdot}05$	
39	2*n*	3627·33	27560·65	$\ldots\ldots\ldots\ldots . u . v+{\cdot}05$	
40	2	3500·314	28560·72	$2X_2 . \ldots\ldots\ldots\ldots +{\cdot}32$	
41	1	3474·574	28772·30	$Y_2 . (2) Q(-a-b+2) . u . v+{\cdot}04$	
42	2*n*	3415·83[5]	29267·10	$X_2 . 2e . u . P_1(-1) . 2v-12y-{\cdot}08$	
43	3	3440·52	29057·08	$Y_1 . \ldots\ldots\ldots\ldots +{\cdot}11$	
44	2*n*	3465·4	28848·4	$X_1 . Y_1 . X_2 . 2e . u . P_1 . 2v-12y+{\cdot}09$	
45	4*n*	3349·287	29848·55	$2X_1 . X_2 . e . u . P_1 . 2v-12y+0$	
46	1	3361·96	29736·01	$Y_1 . Y_2 . 2e . P_1(-2) . 2v-12y-{\cdot}09$	
47		8·45	45·44	$Y_2 . 2e . P_1(-5) . 2v-7y+{\cdot}01$	
		8·11	48·49	$Y_2 . 2e . P_1(-3) . 2v-6y+0$	
		8·04	49·11	$\ldots\ldots\ldots\ldots -5y+{\cdot}03$	
	6	3337·850[6]	29950·82	$Y_2 . 2e . P_1(-3) . 2v-2y+{\cdot}04$	sat. (6)
		7·73	51·90	$X_2 . 2e . P_1(-1) . 2v-5y+{\cdot}10$	
		7·668	52·45	$\ldots\ldots\ldots\ldots -4y+{\cdot}08$	
		7·571	53·32	$Y_2 . 2e . P(-1) . 2v-2y+{\cdot}08$	

[2] E.H. give ... ·01, $n=$... 95·21. The double circle in the map denotes that the mean ... 93·01 is taken.

[3] This formula is deduced direct from (24). If from (17) it is $Y_2(1) Q . e -2y-{\cdot}05$ with $Q=3e.u.P_1.v+{\cdot}80$. They both reduce to $X_2 . 2e . u P_1 . v-4{\cdot}09$.

[4] $133{\cdot}07+124{\cdot}91=2\times128{\cdot}99$ and a on $(-a-b-2)$ shifts 129·15, so that these two lines show parallel inequality and are both displaced a on p_1 and equal and opposite 4·04, or $\pm7y$ within errors.

[5] The link is $v-4{\cdot}07$, the same displacement as in (33, 34); since $-12y=(2)\,s2+{\cdot}02$ the formula may be $X_2 . 2e . u . (2) P_1(-1)2v-{\cdot}06$.

[6] This satelloid in Table I. was found not to be completely subject to the y-rule. It is now seen that the cases which fail are met by a change from X_2 to Y_2 and displacements on p_1.

The P portion (*continued*).

48	2	3610·806	27686·79	$X_2 . Y_2 . u . (1) Q . e - 3y + {\cdot}02$	
49	1.	3629·794	27541·95	$X_2 . (-3) Q(-b-2) - y + {\cdot}01$	
50	1*n*	3721·70	26861·83	$X_2 . u (-3) Q(-b-2) - {\cdot}05$	
51	6	3602·038	27754·18	$(-3) Q(-b-2) - y - {\cdot}03$	sat. (4)
		1·75	6·39	.... $+3y - {\cdot}10$	
52	1*n*	*3664·21*	27284·16	$u . Y_2 . (1) Q(-a-b) . v - {\cdot}11$	
53	2*r*	3805·30	26271·71	$e . Y_2 Q(-2a-b-3) - y - {\cdot}09$	

$D_2(4)$ (2*n*, 3654·3, 27357·2).

I	2	3671·969[7]	27225·62	$(a+3) D_2 + {\cdot}11$
II	1*n*	*3812·08*	26225·81	$e . (a+3) D_2 + {\cdot}10$
III	2	3700·532	27015·48	$Y_1 . (a+3) D_2 + {\cdot}18$

[7] The errors on these are all due to D_2, only measures to ·1. If it is $dn = {\cdot}15$ greater ($d\lambda = -{\cdot}02$) the errors are $-{\cdot}04$, $-{\cdot}05$, $+{\cdot}03$.

Map VII. (D 2.)

Oun shift on $d(2) = {\cdot}3035$.

$D_{12} = 19151{\cdot}63$ (Hasb.) $= {\cdot}46$ (Aretz) ; $D_{11} = 19158{\cdot}370$; $D_{22} = 19399{\cdot}838$ (Fabry & Buisson).

This map is connected with the D(2) lines. It comprises a short chain from D_{11} and a long one connecting D_{12} and D_{22}. The great majority of the lines are from the spark spectrum by Eder and Valenta, with possible O.E. of the order $dn = {\cdot}15$ or over. As the oun shift in $d2$ is ·30, it is always possible to get within ·15 by a suitable choice of these $d2$ displacements, so that where such are involved with the spark lines we can draw no certain or definite conclusions. But some of the lines are much more exact, and conclusions may be drawn with more confidence, *e. g.* (4) in the D_{11} set excludes 681·20 as a real u-link if Aretz is reliable. A very long chain runs from D_{12} to D_{22} in which the links do not annul. There must therefore be at least one false link in it. Again, the line at (9) is a well-known line almost certainly not connected with D(2). It is numerically $D'_{12} . 3u + {\cdot}99$, and if real involving $d_2' - p_1$. Shenstone gives reasons for introducing a new term, and treating it as $\phi - p_1$. The oun shift in $d_2' = 2{\cdot}398$ and in ϕ is 2·669. The parts of the map starting from D_{12} and from D_{22} show clear signs of being real, and the formulæ are calculated for a number of lines from these. Also, the separations from (9) are considered as dependent on $D'_{12}\cdot 3u$ as well as on $\phi-p_1$,, with the result that the latter (Shenstone) and not the D' reproduces the links, and as lines near (9) have good measures the argument is good for the validity of ϕ, as well as for the link values.

If we look at the part from D_{22} back to (25), we recognize the chain to 31 as of normal aspect; then the chain of 4 successive X (25...39) is again a common effect and brings in (25) as a probable D(2) connexion. Again we notice the two parallel inequalities

$$\left.\begin{aligned} 1001\cdot 64 &= e+1\cdot 84 \\ 210\cdot 56 &= X_2-1\cdot 71 \end{aligned}\right\}\text{ from (25),}$$

$$\left.\begin{aligned} 678\cdot 78 &= u-1\cdot 85 \\ 210\cdot 69 &= Y_2-1\cdot 85 \end{aligned}\right\}\text{ from (35);}$$

also the two series inequalities in the long X sets from (25),

$$210\cdot 56+214\cdot 63 = 2Y_2+\cdot 10$$

$$\text{and}\quad 211\cdot 08+210\cdot 69 = 2Y_1+\cdot 08.$$

Since $(-1)D_2(2)$ shifts $1\cdot 23+\cdot 60=1\cdot 83$, we may feel safe in regarding the map between (25) and D_2 as dependent on $D_2(2)$. The formulæ have therefore been calculated for this part in the order D (2), 33, 32, 31, ...

Again starting from (9) = R (say R_1 if $\phi-p_1$, R_2 if $d_2'-p_1+3u$) for $-1000\cdot 88=-e-1\cdot 08$, $(-1)R_1(-3)$ gives $-1\cdot 04$, $(1)R_2(1)$ gives $-1\cdot 17$, in favour of R_1, but the O.E. may be considerable.

$-691\cdot 84=-v+\cdot 24$ and (10) is $v(-1)R_1(-2)+\cdot 04$ (Hasb.) or $+0$ (Aretz), and is not met by R_2. The O.E. is very small, so that R_1 is again good and R_2 impossible. $-212\cdot 24=-X_2+\cdot 03$ and (11) is $X_2 . v . (-1)R_1(-2)+\cdot 07$ (or ·03). The O.E. is not large—see list.

D_{11}.

<table>
<tr><td>1</td><td>2</td><td><i>5232·80</i></td><td>19105·55</td><td>$(b+3)\,D_{11}+\cdot 20$</td></tr>
<tr><td>2</td><td>3</td><td><i>5268·38</i></td><td>18976·51</td><td>$(a+b+4)\,D_{11}+\cdot 12$</td></tr>
<tr><td></td><td colspan="4"><i>a</i>+1 on <i>b</i>+3 gives 128·96 close to observed sep:</td></tr>
<tr><td>3</td><td>2<i>n</i></td><td><i>5282·34</i></td><td>18925·86</td><td>$(a+2b+5)\,D_{11}(-1)-\cdot 11$</td></tr>
<tr><td>4</td><td>1</td><td>5052·485</td><td>19786·741</td><td>$(b+3)\,D_{11}(2) . u+\cdot 16$</td></tr>
</table>

D_{12}.

1	1	*5255·62*	19022·59	$(a+1)\ D_{12}+\cdot 23$
2	1	*5270·13*	18970·21	$(a+b+3)\ D_{12}(-2)+\cdot 08$
3	1*n*	5212·889	19177·89	$(a+b+5)\ D_{12}(-1)\,.\,X_1-\cdot 13$
4	2	*5500·09*	18177·08	$e\,.\,(a+b+6)\ D_{12}(-1)\,.\,X_1+\cdot 08$

5 (2) *5563·83*, 17968·84, 6 (2*n*) *5357·27*, 18661·67, 7 (4) *5418·61*, 18450·41

8	3	*5380·75*	18580·24	$e\,.\,(-1)\ R_1(-3)-\cdot 04$
9	3*n*	5105·543 F.B.	19581·115	$\phi-p_1\equiv R_1$ *or* $d_2'-p_1+3u\equiv R_2$
10	4	5292·539 H.	18889·281	$v\,.\,(-1)\ R_1(-2)+\cdot 04$
11	2	5352·68 H.	18677·05	$X_2\,.\,v\,.\,(-1)\ R_1(-2)+\cdot 07$
12	3	5554·94 H.	17997·01	$X_2\,.\,u\,.\,v\,.\,(2)\ R_1(5)+\cdot 04$
13	3	*5389·70*	18549·39	$X_2\,.\,v\,.\,(-1)\ R_1(-a-1)+\cdot 04$
14	3*n*	*5696·68*	17549·81	$X_2\,.\,v\,.\,(-2)\ R_1(-a)+\cdot 06$
15	1*n*	*5338·19*	18728·38	
16	1*n*	*5639·50*	17727·73	
17	3*n*	*5574·10*	17935·73	
18	2*n*	*5543·11*	18036·02	
19	1*n*	*5760·40*	17355·41	
20	3	*5608·83*	17824·68	
21	1*n*	*5624·71*	17774·37	
22	3	*5666·62*	17642·91	
23	0	*5452·5*	18336	
24	2	*5456·02*	18323·90	
25	4	*5495·12*	18193·52	$X_2\,.\,Y_1\,.\,u\,(2b+4)\ D_{22}(1)-\cdot 06$
26	1*n*	*5440·90*	18374·83	
27	2	*5208·37*	19195·16	$X_2\,.\,Y_1\,.\,u\,(2b+3)\ D_2(3)\,.\,e-\cdot 04$
28	1*n*	*5403·03*	18503·00	$X_2\,.\,Y_1\,.\,u\,.\,v\,.\,(2b+3)\ D_2(3)\,.\,e-\cdot 12$
29	0*n*	5432·071	18404·07	$X_2\,.\,u\,(2b+4)\ D_{22}(2)-\cdot 02$
30	1*n*	*5644·39*	17712·37	$X_2\,.\,u\,.\,v\,(2b+4)\ D_{22}(3)+\cdot 06$
31	3	*5369·63*	18618·71	$u\,.\,(2b+2)\ D_{22}(2)-\cdot 10$
32	1*n*	*5355·10*	18669·24	$u\,.\,(b+1)\ D_{22}(2)-\cdot 03$
33	1*n*	*5340·71*	18719·54	$u\,.\,D_{22}(+1)+\cdot 04$
34	4*n*	*5317·60*	18800·89	$u\,.\,(-a+b-1)\ D_{22}-\cdot 03$
35	2	*5309·41*	18829·79	$u\,.\,(2b+3)\ D_{22}(2)\,.\,X_2-\cdot 06$
36	1*d*	*5124·70*	19508·57	$(2b+4)\ D_{22}\,.\,X_2-\cdot 09$
37	2	5111·945[1] H.	19556·59	$(b+5)\ D_{22}\,.\,X_2-\cdot 05$
38	2	*5295·71*	18878·57	$(b+3)\ D_{22}\,.\,X_2-\cdot 49$
39	0*n*	5250·511	19040·48	$u\,.\,(2b+4)\ D_{22}\ X_2\,.\,Y_2-\cdot 08$ *or* $u\,.\,(2b+4)\ D_2(-1)\,.\,2Y_2-\cdot 05$

F. B. = Fabry and Buisson. H. = Hasbach. Lines in italics are sparks by Eder and Valenta. The others by Aretz.

---

[1] The map is in error, the links being 48·02, 678·02.

Map VIII. (S3.)

$S_1(3)$, $6r$, 4530·843, 22064·79; $S_2(3)$, $6r$, 4480·376, 22313·32.

Oun shift on $s(3)=·203$.

These two linkages give the raw material, but the immediate separations from the S_1, S_2 are clearly no L, M. This cuts off the others, (4) excepted, from S connexions. This is also supported by the facts that (5, 7) are satelloids.

1	4*n*	4539·70	22021·64	8	4	4509·386	22169·77
2	1*n*	4513·20	22151·04	9	4*n*	4697·490	21282·03
3	6*n*	4378·2	22834·0	10	1*n*	4500·37[3]	22214·18
4	6*n*	4674·76	21385·50	11	2*n*	4642·6	21533·6
5	6	4704·598[1]	21249·87	12	2*n*	4794·0	20853·6
		4·20	51·67	13	1	4843·37	20640·95
6	1*n*	4507·5	22179·0	14	2	4797·042	20840·37
7		2·30[2]	88·75	15	2*n*	4767·5	20969·5
		1·986	90·20				
	8	4651·130	21494·15				
		0·73	96·00				
		0·3	97·98				

[1] Is sat. (1).

[2] Is sat. (2).

[3] The separations (10 to 13) are exact Y_2, 680·11, 680·63 within O.E, and $693·25=v+2y$.

The two satelloid sets point to the portions connected with them being P related. The main of (5) and the extreme violet of (7) are separated by 248·11 or the doublet ν within error limits. This suggests that (5) depends on p_2 and (7) on p_1, but their wave numbers as well as those of sat. (3) are so far below the others that any connexion is not evident.

Map IX. ($d_2' - p_1 2 \equiv R$.)

Oun shift on $p(2)=·3241$, on $d_2'=2·398$.

1	8	2766·388	36137·57	4	2*n*	2782·61	35926·89
2	10*r*	2618·381	38180·16	5	2*n*	2786·52	35876·49
3[1]	1	2627·37	38049·61	6	1	2866·19	34878·10

[1] The 130·61 must be a spurious L if the allocation of R is correct.

APPENDIX.

Table A. of shifts on p_1, p_2.

On p_1.	p.		Shifts per oun.	On p_2.
$2a$	31269·24		1·2199	
$4b$	327·90		1·2234	
$a+b$	347·46		1·2246	
$3b$	376·89		1·2262	
a	396·48		1·2274	
$2b$	425·99		1·2291	
b	475·22		1·2320	
0	524·53	p_1	1·2349	$5b$
$-b$	574·00		1·2378	$4b$
	593·81		1·2390	$a+b$
$-2b$	623·54		1·2407	$3b$
	643·41		1·2419	a
$-a$	653·37		1·2425	
$-3b$	673·27		1·2437	$2b$
$-a-b$	703·13		1·2454	
$-4b$	723·08		1·2466	b
$-5b$	772·97	p_2	1·2495	0
$-6b$	823·02		1·2525	$-b$
	873·21		1·2554	$-2b$
	903·36		1·2572	$-a$
	923·47		1·2584	$-3b$
	953·70		1·2602	$-a-b$
	973·87		1·2614	$-4b$
	32024·40		1·2644	$-5b$
	034·54		1·2650	$-2a$
	075·01		1·2674	$-6b$
	125·79		1·2704	$-7b$
	166·52		1·2728	$-3a$
	176·66		1·2734	$-8b$
	227·67		1·2765	$-9b$
	278·80		1·2795	$10b$
	299·26		1·2807	$-4a$
	432·89		1·2887	$-5a$

March, 1926.

H1

XV. *Fluctuation Theory of Scattering of Light in Gases.*
By JAKOB KUNZ, *Ph.D.**

IN a previous article published in this Journal† I have given an elementary theory of the scattering of light by small dielectric spheres. We can consider, however, the phenomenon of scattering of light by the molecules of a gas due to fluctuations of the density of the gas from point to point. It is the purpose of this article to show that the theory of fluctuations can be reduced in part to the previous theory, in which I used essentially the Stokes-Thomson method of determining the radiation of an oscillating charge.

As in the previous article, I assume a plane polarized light-wave proceeding in the z direction.

$$E_x = E_0 \sin 2\pi n\left(t - \frac{z}{v}\right) \quad . \quad . \quad . \quad . \quad (1)$$

through a gas of dielectric constant k. If k were constant we should have a wave of polarization so that

$$P_x = \frac{k}{4\pi} E_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

without scattering. If, however, k varies from the molecules to the vacuum, then we have instead of (2),

$$P_x = \frac{k + \Delta k}{4\pi} E_x. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We can now reduce the present case to the previous one if we add to it a virtual polarization

$$P_v = \frac{\Delta k}{4\pi} E_x. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In other words, if we add to the variable medium a polarization $-P_v$, then the scattering due to the heterogeneous state of the medium will be suppressed. We have, therefore, only to calculate the scattering due to P_v, acting in the volume element $d\tau$ and producing a displacement x in the charge of unit volume. If the charge contained in $d\tau$ is e, then we have

---

* Communicated by the Author.

† Phil. Mag. xxxix. p. 416 (1920).

$$P_v = \frac{e}{d\tau} x = \frac{\Delta k}{4\pi} E_x, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or the displacement

$$x = \frac{\Delta k}{4\pi} \frac{d\tau}{e} E_0 \sin 2\pi t_n ; \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

hence the acceleration

$$f = \frac{d^2x}{dt^2} = -\frac{\Delta k\, d\tau E_0}{4\pi e} (2\pi n)^2 \sin 2\pi n t. \quad . \quad . \quad (7)$$

We assume, further, that the volume element $d\tau$ contains $\nu = N\, d\tau$ molecules, where N is the number of molecules per unit volume. Moreover, we may assume that the small dielectric constant k can be expressed by

$$k = 1 + \alpha N = 1 + \alpha \frac{\nu}{d\tau},$$

denoting by α a constant; then we get

$$\Delta k = \alpha \frac{\Delta \nu}{d\tau}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It has been shown by Sir J. Larmor that the energy radiated by the oscillating charge e per unit time is equal to

$$E_2 = \frac{2}{3} \frac{e^2 f^2}{V^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where V is the velocity of light in the dielectricum k, hence the energy radiated in the time interval dt becomes:

$$dE_2 = \frac{2}{3} \frac{\pi^2}{V^3} E_0^2 \Delta k^2 d\tau^2 n^4 \sin^2 2\pi n t\, dt,$$

and per unit time

$$E_2 = \frac{1}{3} \frac{\pi^2}{V^3} E_0^2 \Delta k^2 d\tau^2 n^4. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Substituting (8) in (10) we obtain

$$E^2 = \frac{1}{3} \frac{\pi^2}{V^3} E_0^2 \Delta \nu^2 n^4 \alpha^2,$$

but $\alpha = \frac{k-1}{N}$, hence

$$E_2 = \frac{1}{3} \frac{\pi^2}{V^3} E_0^2 \frac{(k-1)^2}{N^2} \Delta \nu^2 n^4,$$

and on average

$$\overline{E_2} = \frac{1}{3} \frac{\pi^2}{V^3} E_0^2 \frac{(k-1)^2}{N^2} n^4 \overline{\Delta \nu^2}.$$

A fundamental theorem of the theory of fluctuations states that

$$\overline{\Delta\nu^2} = \nu = N d\tau,$$

hence

$$\overline{E_2} = \frac{1}{3}\frac{\pi^2}{V^3} E_0^2 \frac{(k-1)^2}{N} n^4 \, d\tau. \quad . \quad . \quad . \quad (11)$$

From Poynting's theorem it follows that the energy which flows through unit cross-section per unit time, E_1 is equal to

$$E_1 = \frac{E_0^2 V}{8\pi},$$

or

$$E_0^2 = \frac{8\pi E_1}{V}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Substituting (12) in (11) we obtain

$$\overline{E_2} = \frac{8}{3}\pi^3 \frac{E_1}{V^4} \frac{(k-1)^2}{N} n^4 \, d\tau,$$

but $n = \frac{V}{\lambda}$,

$$\overline{E_2} = \frac{8}{3}\pi^3 E_1 \frac{(k-1)^2}{\lambda^4 N} d\tau.$$

By Maxwell's theory of light, the index γ of refraction is equal to $\sqrt{k}$ or $k-1=\gamma^2-1=2(\gamma-1)$ approximately, hence

$$\overline{E_2} = \frac{32}{3}\pi 3 \frac{E_1(\gamma-1)^2}{\lambda^4 N} d\tau.$$

This is the light energy diffused per unit time from the volume $d\tau = dS\,dz$. This scattered energy corresponds to the difference of the energy which flows in the primary beam through the cross-sections dS and dS', hence

$$\frac{dE_1}{dz} = -\frac{32}{3}\pi^3 \frac{E_1(\gamma-1)^2}{\lambda^4 N} dS,$$

and per unit cross-section

$$\frac{dE_1}{dz} = -\frac{32}{3}\pi^3 E_1 \frac{(\gamma-1)^2}{\lambda^4 N} = -hE_1,$$

or

$$\log E_1 = \log E_0 - hz,$$

or

$$E_1 = E_0 e^{-hz}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where

$$h = \frac{32}{3}\pi^3 \frac{(\gamma-1)^2}{\lambda^4 N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

is the famous coefficient first determined by Lord Rayleigh.

We proceed next to the consideration of a mixed gas whose dielectric constant $k=k_1+k_2-1$, where k_1 and k_2 are the corresponding constants of the two pure gases. If the number of molecules of the two gases in the mixture are n_1 and n_2 per unit volume and the volumes of the molecules v_1 and v_2 respectively, then by Clausius's theory we may write

$$k = 1+3n_1v_1+3n_2v_2,$$

$$\Delta k = 3v_1\Delta n_1+3v_2\Delta n_2,$$

or

$$\Delta k = 3v_1\frac{\Delta\nu_1}{d\tau}+3v_2\frac{\Delta\nu_2}{d\tau},$$

then we obtain from (10)

$$dE_2 = \frac{1}{3}\frac{\pi^2}{V^3}E_0^2(3v_1\Delta\nu_1+3v_2\Delta\nu_2)^2n^4, \quad . \quad . \quad (15)$$

but

$$k_1 = 1+3n_1v_1,$$

$$k_2 = 1+3n_2v_2;$$

hence

$$dE_2 = \frac{1}{3}\frac{\pi^2}{V^3}E_0^2\left(\frac{k_1-1}{n_1}\Delta\nu_1+\frac{k_2-1}{n_2}\Delta\nu_2\right)^2n^4,$$

and on an average

$$\overline{dE_2} = \frac{1}{3}\frac{\pi^2}{V^3}E_0^2\left[\left(\frac{k_1-1}{n_1}\right)^2\overline{\Delta\nu_1^2}+2\frac{(k_1-1)(k_2-1)}{n_1n_2}\overline{\Delta\nu_1}\,\overline{\Delta\nu_2}\right.$$
$$\left.\mp\left(\frac{k_2-1}{n_2}\right)^2\overline{\Delta\nu_2^2}\right]n^4.$$

For a given value $\Delta\nu_1$ we have on an average a positive or negative value $\Delta\nu_2$ with the same probability; hence the double product vanishes, and

$$\Delta\nu = \Delta\nu_1+\Delta\nu_2,$$

$$\overline{\Delta\nu^2} = \Delta\nu_1^2+\Delta\nu_2^2 = \nu_1+\nu_2 = r,$$

by the theorem of fluctuations, mentioned above. $\Delta\nu_1$ and $\Delta\nu_2$ are small numbers. A solution of the last equation is given by

$$\overline{\Delta\nu_1^2} = \nu_1 = n_1\,d\tau,$$

$$\Delta\nu_2^2 = \nu_2 = n_2\,d\tau,$$

hence

$$dE_2 = \frac{1}{3}\frac{\pi^2}{V^3}E_0^2\left[\frac{(k_1-1)^2}{n_1}+\frac{(k_2-1)^2}{n_2}\right]n^4\,d\tau,$$

and by (12)

$$dE_2 = \frac{8\pi^3 E_1}{3\ V^4}\left[\frac{(k_1-1)^2}{n_1}+\frac{(k_2-1)^2}{n_2}\right] n^4\, d\tau,$$

or

$$dE_2 = \frac{8\pi^3}{3} E_1 \left[\frac{(k_1-1)^2}{n_1}+\frac{(k_2-1)_2}{n_2}\right] \frac{1}{\lambda^4}\, d\tau.$$

Again,

$$k_1-1 = 2(\gamma_1-1)\ ; \quad k_2-1 = 2(\gamma_2-1)\ ;$$

$$dE_2 = \frac{32\pi}{3} E_1 \left[\frac{(\gamma_1-1)^2}{n_1}+\frac{(\gamma_2-1)^2}{n_2}\right] \frac{1}{\lambda^4}\, d\tau.$$

From this expression we deduce the coefficient h as before :

$$h = \frac{32\pi^3}{3}\left[\frac{(\gamma_1-1)^2}{n_1}+\frac{(\gamma_2-1)^2}{n_2}\right] \frac{1}{\lambda^4}.$$

This theory leads to the result that the light scattered in a direction at right angles to the primary beam should be completely polarized, because we have considered the molecules as spherical and isotropic particles. But it is well known that even in the case of gases the transversely scattered light is imperfectly polarized. This imperfectness of polarization we may ascribe, with C. V. Raman [*], to the anisotropy of the molecules with varying orientations.

XVI. *On the relation to Physics of the notion of Convergence of Series.* *By* HAROLD JEFFREYS [†].

ENOUGH work has been done on asymptotic and other divergent series to prove that an infinite series may be useful in physical applications without being convergent in the sense defined in works on pure mathematics. It is less generally realized that the converse is equally true, that a series may be convergent and yet be totally useless for the purpose of calculating the value of the function represented. For instance, the exponential series for e^{-1000} is convergent in the mathematical sense ; but it cannot be used to evaluate the quantity it denotes, for its terms increase rapidly up to the thousandth, which would have to be evaluated to over 870 significant figures, a quite unpracticable number.

The fact is that convergence and utility are not the same thing, and are essentially unconnected. In evaluating a function one is limited to expansions that can be actually summed numerically in the time available, and it is therefore necessary that the first few terms shall give a good approximation to the function. These terms once obtained, the rest of the series is of no further interest to the physicist. The mathematical definition of convergence, on the other hand, depends on whether the sum S_n of the first n terms tends to a finite limit as n tends to infinity, and the criterion for the existence of such a limit depends only on the later terms.

---

[*] C. V. Raman, Phil. Mag. xlv. p. 213 (1923).

[†] Communicated by the Author.

The distinction recalls that arising in the theory of scientific inference in connexion with the possibility of a deductive theory not involving the notion of probability *. Deductive theories of scientific knowledge are usually based on the notion of infinite classes of data, or on that of a limit, which again implicitly involves infinite classes. Hence they are inapplicable to actual knowledge, which is necessarily in point of fact based on a finite number of data. The summation of a series, in the mathematical sense, could be carried out only by a being with infinite time at his disposal.

The definition of an asymptotic approximation, indeed, is nearer to the physicist's needs than is that of convergence. Such a definition is † that a series S is an asymptotic expansion of a function $f(z)$ if for all values of n

$$\operatorname*{Lim}_{z \to \infty} | z^n\{ f(z) - S_n(z) \} | = 0.$$

The definition emphasizes the importance of the early terms of the series, and it is on the possibility of evaluating these that the usefulness of the expansion depends. It still, however, involves the notion of a limit when z tends to infinity; the physicist is concerned rather with the actual values of $f(z)$ and $S_n(z)$ for finite values of z, and needs more a specification of some value not exceeded by $|z^n\{f(z) - S_n(z)\}|$ within the range of values of z that he contemplates ‡.

A similar point arises in relation to certain series ordinarily regarded by the pure mathematician as slowly convergent. For instance, the exact sum of the series $\sum\limits_{n=1}^{\infty} n^{-4}$ is known to be $\frac{1}{90}\pi^4$, or 1·081. The sum of the first four terms is 1·079, so that an accuracy of about 0·2 per cent. is achieved by taking only four terms. The series is usually considered slowly convergent because the ratio of consecutive terms tends to unity when n tends to infinity, but for physical purposes the rapid decrease of the early terms makes the series a very useful approximation.

---

* Wrinch and Jeffreys, Phil. Mag. xlii. pp. 369–390 (1921).

† Whittaker and Watson, 'Modern Analysis,' 8.2.

‡ *E. g.*, Whittaker and Watson point out that $n!/z$ is such a quantity in an illustrative example given by them.

The belief that convergence has something to do with physical utility may have arisen from the fact that the simplest series possessing either property are geometrical series, which are accordingly prominent in all discussions of both properties. But it is easy to find series possessing either property without the other, and it is well to specify as clearly as possible which one is being considered.

A further point of some importance is that a finite number of terms may be a good approximation to a function without being also a set of terms from a series of terms of the same form that represents the function exactly. The question has arisen in connexion with an approximate solution by Stoneley [*] of the problem of the straining of the earth by bodily forces. The stresses everywhere must be continuous, but as there is a discontinuity of the elastic properties at an internal layer the first derivatives of the displacements must be discontinuous. In principle, apart from matters peculiar to the special problem, the method has been to find two polynomials of the sixth degree in the distance from the centre such that the energy is a minimum for small variations in the coefficients. The actual state of equilibrium being such as to make the energy a minimum, the success of the method depends on the possibility of representing the displacement with sufficient accuracy by a polynomial of the assumed degree. As this is precisely the principle of ordinary interpolation, there seemed to be little doubt on the point until it was found that in the solution the coefficients of the terms of higher degrees were very much the greatest, making it clear that the polynomial was not the beginning of a convergent power series. It was, indeed, demonstrable *a priori* that the exact solution could not be expressed as a convergent power series, for such a series has a continuous differential coefficient at every point within its circle of convergence, whereas the solution in Stoneley's problem had a first derivative discontinuous at one point.

An analogue involving the same principle in a simpler form is provided by the electrostatic problem, in one dimension, of two plates at $x = \pm 1$, at potentials 0 and 1 respectively, the medium having dielectric constant 1 between $x = -1$ and $x = 0$, and 2 from $x = 0$ to $x = 1$. The exact solution is easily found to be

$$\begin{aligned} V &= \tfrac{2}{3}(1+x) \qquad && -1 < x < 0 \\ V &= \tfrac{2}{3} + \tfrac{1}{3}x \qquad && 0 < x < 1. \end{aligned}$$

Now since V within the range considered is a function with limited total fluctuation it is necessarily expressible over the whole range as a convergent series of Legendre polynomials in x. It follows that a solution to any required degree of accuracy can be found by taking enough terms of this series. But the sum of a finite number of polynomials can be rearranged as a single polynomial. Hence a solution to any degree of accuracy can be obtained as a polynomial, and the fundamental hypothesis of Stoneley's method is justified. But the coefficients of the same power of x in successive approximations do not tend in the limit to equality with the terms of a convergent power series; or indeed to any limit at all. If we assume

---

[*] M. N. R. A. S., Geoph. Suppt. i. (1926).

$$V = \sum_{n=0}^{\infty} A_n P_n(x),$$

we find by the usual methods

$$A_0 = \tfrac{7}{12}\,; \quad A_1 = \tfrac{1}{2},$$

and for later terms,

$$A_{2m-1} = 0\,; \quad A_{2m} = -\frac{4m+1}{6\,.\,2^{2m}}\,\frac{(2m-2)\,!}{(m+1)\,!\,(m-1)\,!}.$$

On applying Stirling's approximation we find without difficulty that when m is large A_{2m} is nearly $-\dfrac{1}{6\sqrt{\pi}}m^{-\frac{3}{2}}$. The Legendre functions never exceed unity, and the series therefore converges. Also its terms decrease rapidly at the beginning and steadily thereafter, so that it provides a useful approximation. A_6 is $-13/768$ and A_8 nearly $-0{\cdot}01$; the error in stopping at P_6 is therefore of the order of one or two per cent. The error of a polynomial approximation including x^6 will of course be the same.

But the coefficient of x^n in P_n is $(2n)\,!/2^n(n\,!)^2$, which is, by Stirling's approximation, equivalent to $2^n/\sqrt{(\pi n)}$. If we stop at x^{2m}, the coefficient of the highest power of x retained will be asymptotically equivalent to $2^{2m-\frac{3}{2}}/3\pi m^2$, which increases indefinitely with m.

The large values found by Stoneley for the later coefficients in his polynomials are therefore inherent in the form of approximation adopted, but do not thereby imply that the approximation is unsatisfactory. The polynomials are not correctly regarded as the beginning of power series, but as the rearranged early parts of Legendre series, which must be convergent and also suitable for computation. It is true, of course, as is pointed out by Stoneley, that the large later coefficients must be computed with the full absolute accuracy required for the earlier ones, but this is a matter of convenience and had to be weighed against others.

XVII. *Professor Lees' Criticism of 'The Surface History of the Earth.'* *By* Prof. J. Joly, *M.A., D.Sc., F.R.S.*[*]

IN his review of my book (Phil. Mag. April 1926) Professor Lees sets forth certain difficulties which he says have to be overcome before the general theory involved can be accepted.

"One of these (difficulties)," he says, "is the concentration of the surplus heat from radioactive changes in a particular layer." If I apprehend Prof. Lees' objection rightly, the answer is that such a concentration forms no part of my theory. On the contrary, care is taken to guard against such an inference. I say (pp. 76–78): "It seems probable from these facts (*i. e.* the lesser radioactivity of the ultrabasic rocks and the very feeble radioactivity of meteorites) that the radioactivity of the Magma is succeeded by the lesser radioactivity of an ultrabasic layer which may reach to a depth of several hundred miles from the earth's surface. Further down the great core of the earth probably possesses much smaller quantities of the heat-producing elements. But this is surmise." The intervention of deep-seated radioactive heat at long intervals in connexion with certain major revolutions is also referred to not only in my book but in all I have written upon the subject. And, of course, the development of heat in the continental layer is frequently referred to. In a word, it is a leading feature of the theory that the arbitrary distribution of the radioactive elements is not only unnecessary but would give rise to difficulties. And this fact constitutes one of its claims to credibility.

After making this objection Prof. Lees immediately continues: "and another the secular rise of temperature of the earth during the whole of its past history owing to the amount of radioactive material postulated."

Upon this point I say (p. 76):—"If the natural question be asked:—'Does this source of heat also extend into the interior'?—we must answer that such evidence as we possess suggests an interior resembling the nickeliferous iron of the meteorite. Meteoric iron sometimes contains a minute trace of radium and therefore of uranium. The thorium content of metallic meteorites has not been investigated." This is the amount of interior radioactivity postulated.

Is there any difficulty raised here that does not affect any conceivable theory of earth-history based upon the facts at our disposal? We are up against the unknown and unknowable. But I think we would justifiably infer that the earth may be too young—even according to the greater estimates of geological time—to reveal any surface effects arising out of so feeble an interior radioactivity; and it is with its surface history that we are concerned.

---

[*] Communicated by the Author.

Professor Lees continues: "The author unfortunately bases his calculations of the expansion in melting of the rocks 70 miles below the surface on the 10 per cent. increase of volume found when rocks melt at atmospheric pressure," etc.

This, however, is not the case.

The figures quoted are used in an early paper of mine (Phil. Mag. June 1923). The 10 per cent. expansion is not supposed to occur 70 miles down, but is the suggested average volume-change (*loc. cit* p. 1180). an explanation and a warning being added:—"As regards the estimated magnitude of this expansional effect, the amount of the voluminar expansion assumed is, to some extent, arbitrary. The upper part of the Magma may, indeed, enlarge or contract by some 10 per cent. of its volume in changing from solid to liquid and *vice versa*. The volume-change of the deeper parts is unknown, but if—as appears probable—there is vertical circulation of super-heated material, the volume-change may be considerable. The assumption of a mean change of 10 per cent. may, however, be somewhat excessive" (p. 1181).

In the book which Professor Lees is reviewing, a deeper basaltic substratum is considered and an average volume-change of 7 per cent. is assumed. This involves an allowance of five-twelfths for the average pressure effect; for, as pointed out in the early paper (referred to above) appearing in this Journal, and also in 'The Surface History of the Earth,' the experimentally determined volume-change of diabase from crystalline solid to liquid is 12 per cent. (not 10 per cent.).

I think it will be apparent from what I have stated that the two difficulties specially raised by Professor Lees are, in point of fact, non-existent. The calculation of volume-change of the substratum has been as fully considered as the available data permitted; but—and this is additional to what has appeared in my book—recent statements by high authorities on the subject of crustal shortening attending the revolutions and on the number of the revolutions would seem to permit of lower estimates of the depth of the substratum involved or of its average volume-change or of both.

I hope to revert to this subject at a later date.

April 6th, 1926.

XVIII. *Orthogonal Potentials.* *By* P. J. Daniell, *Sc.D.**

IN this paper are introduced what we call orthogonal potentials as an aid in applying the minimum energy method to some simple problems in elasticity and hydrodynamics. The particular advantage gained is that we can apply the formulæ directly to any particular case by the substitution of numerical values which depend only on second and higher moments which are themselves calculable by simple quadratures.

In the first part of the paper we confine our attention to two-dimensional problems in which a function $f(x, y)$ is to be found satisfying Laplace's equation $\Delta f=0$ within the area A and taking on given values $f(x, y)=a(x, y)$ on the boundary B of A. We assume that the boundary is so simple that the minimum energy method will lead, if properly used, to an approximate solution of the problem; so that we neglect the difficulties which would be raised by the mathematical purist.

A potential, $f(x, y)$, is a function possessing second-order derivatives and satisfying

$$\Delta f=\partial^2 f/\partial x^2+\partial^2 f/\partial y^2=0$$

throughout the interior of A.

We define the *potential-product* of two potentials, f, g, as

$$[f\cdot g]=\int\left(\frac{\partial f}{\partial x}\frac{\partial g}{\partial x}+\frac{\partial f}{\partial y}\frac{\partial g}{\partial y}\right)dA\div A,$$

integrating over the area A and dividing by the whole area A.

Two potentials, f, g, are said to be *orthogonal* if their potential-product is zero, *i. e.* if

$$[f\cdot g]=0.$$

A set of potentials, $\phi_1, \phi_2, \ldots$, is said to be *normal* if

$$\begin{aligned}[\phi_i\cdot\phi_j]&=0, \quad i\neq j,\\ &=1, \quad i=j.\end{aligned}$$

A set of potentials, $\phi_1, \phi_2, \ldots$, is said to be *complete* if there is no continuous potential ψ (other than a constant) such that for all values of i,

$$[\phi_i\cdot\psi]=0.$$

In the same way as in the case of orthogonal sets of functions in the more usual sense, it is possible, given a complete set of linearly independent potentials, to form from them by linear combinations a complete and normal set of potentials.

---

* Communicated by the Author.

In the first place, given any potential, g, we can normalize it by introducing a factor α, α being the reciprocal of the square-root of $[g \cdot g]$.

Let $g_1, g_2, \ldots$ be a complete set of potentials, and take

$$f_1=\alpha_1 g_1, \quad f_2=\alpha_2(g_2-f_1[g_2 \cdot f_1]),$$

$$f_3=\alpha_3(g_3-f_1[g_3 \cdot f_1]-f_2[g_3 \cdot f_2]),$$

$$f_n=\alpha_n(g_n-f_1[g_n \cdot f_1]-f_2[g_n \cdot f_2]- \ldots \ldots -f_{n-1}[g_n \cdot f_{n-1}]),$$

where $\alpha_1, \alpha_2, \ldots \alpha_n, \ldots$ are the factors which normalize $f_1, f_2, \ldots f_n, \ldots$ It can readily be proved that f_2 is orthogonal to f_1, and that if $f_1, f_2, \ldots f_{n-1}$ are orthogonal to one another. f_n is orthogonal to all of them. Furthermore, since the f's now form a normal set,

$$\alpha_n^2([g_n \cdot g_n]-[f_1 \cdot g_n]^2- \ldots -[f_{n-1} \cdot g_n]^2)=1.$$

By the usual form of Green's theorem, if f and g are potentials,

$$\mathrm{A}[f \cdot g]=\int f \partial g/\partial n \, ds=\int g \partial f/\partial n \, ds,$$

integrating round the boundary B of A, when δn is an element of normal *outwards* from A.

Indeed, provided only that g be a potential,

$$\mathrm{A}[f \cdot g]=\int f \partial g/\partial n \, ds.$$

If f is a potential and $\phi_1, \phi_2, \ldots$ a normal set of potentials, let

$$c_n=[f \cdot \phi_n],$$

$$f_n=c_1\phi_1+c_2\phi_2+ \ldots +c_n\phi_n.$$

Then

$$[(f-f_n) \cdot (f-f_n)]=[f \cdot f]-2c_1[f \cdot f_1]- \ldots -2c_n[f \cdot f_n] + c_1^2+ \ldots +c_n^2,$$

$$=[f \cdot f]-(c_1^2+ \ldots +c_n^2).$$

But, by definition, for any g, $[g \cdot g]$ is non-negative, so that

$$c_1^2+c_2^2+ \ldots +c_n^2 \leqq [f \cdot f].$$

It follows that

$$c_1^2+c_2^2+ \ldots$$

is either a finite or a converging series, and hence that

$$g=c_1\phi_1+c_2\phi_2+ \ldots$$

exists *. Furthermore

$$[(f-g) \cdot \phi_n]=[f \cdot \phi_n]-[g \cdot \phi_n]=c_n-c_n=0.$$

---

* A proof is possible in the case of areas of a certain simplicity, but our present interest is in the applications.

Hence, if the set $\phi_1, \phi_2, \ldots$ is *complete* as well as normal,

$$c_1\phi_1 + c_1\phi_2 + \ldots$$

determines the true solution f, except for an additive constant. But on the boundary

$$f(x, y) = a(x, y)$$

is given, so that

$$c_n = [f \cdot \phi_n] = \int f \partial\phi n/\partial n \, ds/\mathrm{A},$$
$$= \int a \partial\phi_n/\partial n \, ds/\mathrm{A}$$

is known, and the solution, f, is completely determined.

Also if $a(x, y)$ is known, not only on the boundary B but also throughout A, and possesses first derivatives,

$$c_n = \int\left(\frac{\partial a}{\partial x}\frac{\partial \phi_n}{\partial x} + \frac{\partial a}{\partial y}\frac{\partial \phi_n}{\partial y}\right)d\mathrm{A}/\mathrm{A}.$$

In particular if, as in the cases to be considered,

$$a = \tfrac{1}{2}(x^2 + y^2),$$
$$c_n = \int\left(x\frac{\partial \phi_n}{\partial x} + y\frac{\partial \phi_n}{\partial y}\right)d\mathrm{A}/\mathrm{A}.$$

In an actual case it will be necessary to choose a suitable set of potentials $g_1, g_2, \ldots$, and then to determine the corresponding normal set. After that the constants $c_1, c_2, \ldots$ will be evaluated, but it will be unnecessary to proceed beyond a certain stage, since the assumptions made in reducing the actual problem to a simple mathematical form will introduce errors of appreciable magnitude.

Polynomial Potentials.

We are given the area A, and we shall choose axes of coordinates passing through the centre of area and so as to be principal axes for second moments. That is to say, we shall have

$$\int x d\mathrm{A} = \int y d\mathrm{A} = \int xy d\mathrm{A} = 0.$$

Let k^2 be the square of the polar radius of gyration,

$$k^2 = \int(x^2 + y^2)d\mathrm{A}/\mathrm{A},$$
$$\lambda = \int(x^2 - y^2)d\mathrm{A}/\mathrm{A}k^2,$$

so that λ is a pure number between ± 1. For an ellipse of semi-axes a, b or a rectangle of sides $2a$, $2b$,

$$\lambda = (a^2 - b^2)/(a^2 + b^2).$$

It can be verified that

$$\phi_1 = x, \quad \phi_2 = y, \quad \phi_3 = (x^2 - y^2)/2k, \quad \phi_4 = xy/k$$

form, so far, a normal set.

Since they are each homogeneous, the constants c_1, c_2, etc., can easily be found. Indeed,

$$c_1 = c_2 = c_4 = 0,$$
$$c_3 = 2\int \phi_3 dA/A = \int (x^2 - y^2) dA/Ak = \lambda k.$$

Hence

$$f_4 = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$$
$$= \lambda(x^2 - y^2)/2.$$

This formula would be exact for an ellipse of semi-axes a, b.

For the cubic terms take

$$v_5 = \tfrac{1}{3}x^3 - xy^2, \quad v_6 = x^2y - \tfrac{1}{3}y^3,$$

and let

$$\int v_5 dA/A = k^2\beta_5, \quad \int v_6 dA/A = k^2\beta_6,$$
$$\int x(x^2 + y^2) dA/A = k^2\xi, \quad \int y(x^2 + y^2) dA/A = k^2\eta,$$
$$\int (x^2 + y^2)^2 dA/A = k^4\rho^2.$$

Then

$$[\phi_1 \,.\, v_5] = [\phi_2 \,.\, v_6] = \lambda k^2,$$
$$[\phi_2 \,.\, v_5] = -[\phi_1 \,.\, v_6] = 0,$$
$$[\phi_3 \,.\, v_5] = [\phi_4 \,.\, v_6] = k\xi,$$
$$[\phi_4 \,.\, v_5] = -[\phi_3 \,.\, v_6] = k\eta,$$
$$[v_5 \,.\, v_6] = 0, \quad [v_5 \,.\, v_5] = [v_6 \,.\, v_6] = k^4\rho^2.$$

Hence

$$\phi_5 = [\tfrac{1}{3}x^3 - xy^2 - \lambda k^2 x - \xi(x^2 - y^2)/2 + \eta xy]/k^2\rho',$$
$$\phi_6 = [x^2y - \tfrac{1}{3}y^3 - \lambda k^2 y - \eta(x^2 - y^2)/2 - \xi xy]/k^2\rho',$$

where

$$(\rho')^2 = \rho^2 - \lambda^2 - (\xi^2 + \eta^2)/k^2$$

Also

$$x\partial v_5/\partial x + y\partial v_5/\partial y = 3v_5, \text{ etc.}$$

Hence

$$c_5 = (3\beta_5 - \lambda\xi)/\rho',$$
$$c_6 = (3\beta_6 - \lambda\eta)/\rho',$$

$$f_6 - f_4 = c_5\phi_5 + c_6\phi_6$$
$$= (3\beta_5 - \lambda\xi)[\tfrac{1}{3}x^3 - xy^2 - \lambda k^2 x - \xi(x^2 - y^2)/2 + \eta xy]/\rho'^2k^2$$
$$+ (3\beta_6 - \lambda\eta)[x^2y - \tfrac{1}{3}y^3 - \lambda k_2 y - \eta(x^2 - y^2)/2 - \xi xy]/\rho'^2k^2.$$

The corresponding exact forms of the fourth degree are so complicated that it is advisable to make some simplifying assumption. In practice, unless the cubic terms are very small—when, for example, there is practical symmetry about each of the two axes—the fourth-order terms will only give a small correction. In either case very little error is introduced by calculating the fourth-order terms as if the third-order constants were negligible. Hence we now take

$$\beta_5 = \beta_6 = \xi = \eta = 0,$$

$$\phi_5 = (x^3/3 - xy^2 - \lambda k^2 x)/k^2\rho',$$

$$\phi_6 = (x^2 y - y^3/3 - \lambda k^2 y)/k^2\rho'.$$

Take

$$v_7 = (x^4 - 6x^2y^2 + y^4)/4, \quad v_8 = x^3 y - xy^3,$$

and let

$$\int v_7 dA/A = k^4\beta_7, \quad \int v_8 dA/A = 0,$$

$$\int xy^3 dA = \int x^3 y dA = 0,$$

$$\int (x^4 - y^4) dA/A = \lambda' k^4,$$

$$\int (x^2 + y^2)^3 dA/A = \sigma^2 k^6.$$

Then

$$\partial v_8/\partial x = 3x^2 y - y^3 = -\partial v_7/\partial y,$$

$$\partial v_8/\partial y = x^3 - 3xy^2 = +\partial v_7/\partial x,$$

$$[\phi_1 . v_7] = [\phi_2 . v_8] = [\phi_2 . v_7] = -[\phi_1 . v_8] = 0,$$

$$[\phi_3 . v_7] = [\phi_4 . v_8] = \lambda' k^3,$$

$$[\phi_4 . v_7] = -[\phi_3 . v_8] = 0,$$

$$[\phi_5 . v_7] = [\phi_5 . v_8] = [\phi_6 . v_7] = -[\phi_5 . v_8] = 0,$$

$$[v_7 . v_8] = 0, \quad [v_7 . v_7] = [v_8 . v_8] = \sigma^2 k^6.$$

Hence

$$\phi_7 = [(x^4 - 6x^2y^2 + y^4)/4 - \lambda' k^2 (x^2 - y^2)/2]/k^3\sigma',$$

$$\phi_8 = [x^3 y - xy^3 - \lambda' k^2 xy]/k^3\sigma',$$

where

$$(\sigma')^2 = \sigma^2 - \lambda'^2.$$

Also

$$c_7 = (4\beta_7 - \lambda\lambda')k/\sigma', \quad c_8 = 0,$$

$$f_8 - f_6 = c_7\phi_7 + c_8\phi_8$$

$$= (4\beta_7 - \lambda\lambda')[(x^4 - 6x^2y^2 + y^4)/4 - \lambda' k^2 (x^2 - y^2)/2]/k^2\sigma'^2.$$

Application to Torsion [*].

If θ is the twist, l the length of the rod, n the modulus of rigidity, the resultant couple Q is given by

$$Q=n\left(\frac{\theta I}{l}-\int\left(x\frac{\partial\psi}{\partial x}+y\frac{\partial\psi}{\partial y}\right)dA\right)$$

where $\Delta\psi=0$ throughout A and

$$\psi=\theta(x^2+y^2)/2l$$

on the boundary. Put $\psi=\theta\phi/l$ so that, on the boundary,

$$\phi=\tfrac{1}{2}(x^2+y^2).$$

Then ϕ is the solution obtained above, and

$$Q=\frac{n\theta}{l}\left(I-\int\left(x\frac{\partial\phi}{\partial x}+y\frac{\partial\phi}{\partial y}\right)dA\right)$$

$$=\frac{n\theta}{l}\left(I-\Sigma_i c_i\int\left(x\frac{\partial\phi_i}{\partial y}+y\frac{\partial\phi_i}{\partial y}\right)dA\right)$$

$$=n\theta(A/l)(k^2-\Sigma_i c_i^2)=\kappa n\theta I/l.$$

In general, if the area does not depart too far from the circular or elliptic, the terms in c_3, c_4 will be the most important, and c_7, c_8 are small terms in which we can make approximating assumptions without fear of great error. In view of Saint Venant's approximate formula (p. 177),

$$Q=n\theta A^4/40Il,$$

it is convenient to express κ in the form

$$\kappa=fA^4/40I^2=fA^2/40k^4,$$

so that

$$f=40\kappa(k^2/A)^2$$

and is a pure number not far from 1.

Substituting the values of the c's,

$$\kappa=1-\lambda^2-[(3\beta_5-\lambda\xi)^2+(3\beta_6-\lambda\eta)^2]/k^2\rho'^2$$
$$-(4\beta_7-\lambda\lambda')^2/\sigma'^2$$

to this order of approximation.

Illustrations.—Ellipse.

In this case, by symmetry, $\beta_5=\beta_6=\xi=\eta=0$,

$$Ak^4(4\beta_7-\lambda\lambda')=\int(x^4-6x^2y^2+y^4)dA-\lambda\int(x^4-y^4)dA$$
$$=A[c_4(a^4+b^4)-6c_2a^2b^2-\lambda c_4(a^4+b^4)],$$

where c_4, c_2 are the average values of x^4, x^2y^2 for a unit circle. But for a circle

---

[*] The references will be to Prescott, 'Applied Elasticity,' as here, p. 140.

$$2c_4 - 6c_2 = \text{average of } r^4\cos 4\theta = 0\,;$$

$$\begin{aligned} k^4(4\beta_7 - \lambda\lambda') &= c_4[(a^4+b^4-2a^2b^2) - \lambda(a^4-b^4)] \\ &= c_4(a^2-b^2)[(a^2-b^2) - \lambda(a^2+b^2)] = 0. \end{aligned}$$

Hence, as we knew beforehand, the third- and fourth-order terms disappear. Indeed, the second terms give an exact solution, and

$$\kappa = 1 - \left(\frac{a^2-b^2}{a^2+b^2}\right)^2 = \frac{4a^2b^2}{(a^2+b^2)^2} = \frac{1}{4\pi^2}\,\frac{A^2}{k^4},$$

$$f = 40/4\pi^2 = 1{\cdot}01.$$

Rectangle.

In this case, again by symmetry,

$$\beta_5 = \beta_6 = \xi = \eta = 0,$$

$$\lambda = (a^2-b^2)/(a^2+b^2), \quad k^2 = (a^2+b^2)/3,$$

$$k^4(4\beta_7 - \lambda\lambda') = \int(x^4 - 6x^2y^2 + y^4)dA/A - \lambda\int(x^4-y^4)dA/A,$$

$$4\beta_7 - \lambda\lambda' = -12a^2b^2/5(a^2+b^2)^2,$$

$$\lambda' = 9\lambda/5,$$

$$\sigma^2 = 27[(a^6+b^6)/7 + a^2b^2(a^2+b^2)/5]/(a^2+b^2)^3,$$

$$= 27(3+2\lambda^2)/35,$$

$$\sigma'^2 = 27(15-11\lambda^2)/175,$$

$$\kappa = (1-\lambda^2) - 112a^4b^4/3(15-11\lambda^2)(a^2+b^2)^4,$$

$$f = \frac{10}{9}\left[1 - \frac{7}{3}\,\frac{1-\lambda^2}{15-11\lambda^2}\right]$$

$$= 1 - \frac{5 - 7{\cdot}4\lambda^2}{27(3-2{\cdot}2\lambda^2)}.$$

For a square $a=b$, $\lambda=0$, and

$$f = 1 - 5/81 = 0{\cdot}938,$$

while Prescott's result (from p. 153) is

$$f = 0{\cdot}937.$$

If $b=2a$, $\lambda = -0{\cdot}6$,

$f = 0{\cdot}961$ (Prescott, $0{\cdot}953$).

If $b=4a$, $\lambda = -0{\cdot}8824$,

$f = 1{\cdot}022$ (Prescott, $0{\cdot}995$).

The two values are identical when $b/a = \infty$, namely 10/9. However, it must be remembered that Prescott's method for the rectangle could not be applied to any other shape; whereas our method is equally suitable for any compact area and is the result of applying a minimum energy method assuming a fourth-power function only.

Isosceles Triangle.

Take the x-axis to be the symmetric median of the triangle, $3h$ being the length of this median, and let the length of the perpendicular side be $2a$. In the case of an equilateral triangle,

$$a=\sqrt{3}h.$$

We shall neglect the fourth-order terms. Also on account of the symmetry about the x-axis,

$$\beta_6=\eta=0,$$
$$\mathrm{A}=3ah, \quad k^2=(3h^2+a^2)/6,$$
$$\lambda=(3h^2-a^2)/(3h^2+a^2).$$

We observe that λ is zero for an equilateral triangle which agrees with the fact that for such an area the second momental ellipse reduces to a circle.

$$\beta_5=2h(h^2+a^2)/5(3h^2+a^2)=2k(2-\lambda)\sqrt{(1+\lambda)/15},$$
$$\xi=2h(3h^2-a^2)/(3h^2+a^2)=2k\lambda\sqrt{(1+\lambda)/5},$$
$$\rho^2=12(9h^4+2a^2h^2+a^4)/5(3h^2+a^2)^2=4(2+\lambda^2)/5,$$
$$\rho'^2=(40-9\lambda^2-4\lambda^3)/25,$$
$$3\beta_5-\lambda\xi=2k(2-\lambda-\lambda^2)\sqrt{(1+\lambda)/5},$$
$$\kappa=3(1-\lambda^2)\frac{8+\lambda^2}{40-9\lambda^2-4\lambda^3},$$

or, approximately, if λ^2 is small,

$$f=\frac{8}{9}\left(1+\frac{7\lambda^2}{20}+\frac{\lambda^3}{10}\right).$$

For an equilateral triangle λ is zero,

$$f=8/9=0{\cdot}889,$$

which corresponds to the value obtained by Prescott (p. 177). In fact, in this case, the potential is of the third degree, so that our approximation is exact.

For a right-angled isosceles triangle, $a=3h$,

$$\lambda=-1/2,$$
$$f=1-2/45=0{\cdot}96,$$

while if $h=a$ so that the semi-vertical angle of the triangle is arc tan 1/3,

$$f=0{\cdot}98.$$

Application to Viscous Flow.

If the pressure difference is p, the length of the tube l and the coefficient of viscosity η, then

$$p/l=\eta\Delta w$$

throughout A, while on the boundary

$$w=0.$$

Put

$$w=p[\tfrac{1}{2}(x^2+y^2)-\phi]/2l\eta\,;$$

then throughout A, $\Delta\phi=0$ and on the boundary

$$\phi=(x^2+y^2)/2,$$

so that ϕ is the same function as that found in the case of torsion. The total rate of flow is

$$\begin{aligned}\mathrm{Q}=\int w\,d\mathrm{A}&=[p/2l\eta]\,[\tfrac{1}{2}\mathrm{I}-\int\phi\,d\mathrm{A}]\\&=\frac{p}{2l\eta}(\tfrac{1}{2}\mathrm{I}-\Sigma_i c_i\int\phi_i\,d\mathrm{A}).\end{aligned}$$

Now $c_1=c_2=0$ and ϕ_3, ϕ_4 are homogeneous of the second degree, so that

$$c_3=2\int\phi_3\,d\mathrm{A}/\mathrm{A},\quad c_4=2\int\phi_4\,d\mathrm{A}/\mathrm{A}=0.$$

Then, as far as the second-order terms,

$$\mathrm{Q}=p(\mathrm{I}-\mathrm{A}c_3{}^2)/4l\eta=p\mathrm{I}(1-\lambda^2)/4l\eta.$$

ϕ_5, ϕ_6 are not homogeneous, but differ from homogeneous expressions of the third order by linear terms whose integrals vanish, and quadratic terms with small integrals when the tube is of comparatively compact shape. Hence we may take, approximately,

$$c_5=3\int\phi_5\,d\mathrm{A}/\mathrm{A},$$

and similar results for c_6 and the fourth-order terms. Hence we may take

$$\mathrm{Q}=(p\mathrm{A}/4l\eta)[k^2(1-\lambda^2)-2(c_5{}^2+c_6{}^2)/3-(c_7{}^2+c_8{}^2)/2].$$

Indeed, if we only desire a rough approximation, we can again use Saint Venant's formula and obtain

$$\mathrm{Q}=\frac{p\mathrm{A}^4}{160l\eta\mathrm{I}}.$$

Three Dimensions.

There is not space in this paper to consider the application of the method to three-dimensional problems in general, but we can give a few indications of the development.

The body equations[*] are

$$m\,\partial\Delta/\partial x+n\nabla^2 u+\rho X=0,$$

and two similar equations. At the surface the equations for a free body are

$$\lambda[(m-n)\Delta+2n\partial u/\partial x]+\mu[n(\partial v/\partial x+\partial u/\partial y)]$$
$$+\nu[n(\partial u/\partial z+\partial w/\partial x)]=0,$$

together with two similar equations, where λ, μ, ν are the direction-cosines of the normal to the surface.

Let ϕ denote a vector displacement field (u, v, w) and let ϕ' denote the corresponding stress tensor $(P_1, P_2, P_3, S_1, S_2, S_3)$,

$$P_1=(m-n)\Delta+2n\partial u/dx,$$
$$S_1=n(\partial w/\partial y+\partial v/\partial z)$$

$(\phi')_n$ denotes the vector force obtained by combining ϕ' with the direction (λ, μ, ν), so that the x-component of $(\phi')_n$ is

$$\lambda P_1+\mu S_3+\nu S_2.$$

Moreover, $\psi\,.\,(\phi')_n$ is the scalar product of the vectors ψ and $(\phi')_n$.

Let $E(\phi\,.\,\phi)$ denote the elastic energy per unit volume due to the displacement $\phi=(u, v, w)$. Then[*]

$$2E(\phi\,.\,\phi)=P_1\alpha+P_2\beta+P_3\gamma+S_1a+S_2b+S_3c$$
$$=\phi'\,.\,\phi'',$$

where ϕ' is the above stress tensor corresponding to ϕ, while ϕ'' is the strain tensor $(\alpha, \beta, \gamma, a, b, c,)$,

$$\alpha=\partial u/\partial x,\quad a=\partial v/\partial z+\partial w/\partial y, \text{ etc.}$$

Similarly, we define

$$2E(\phi\,.\,\psi)=\phi'\,.\,\psi''=\phi''\,.\,\psi'$$

and $$W(\phi\,.\,\psi)=2\int E(\phi\,.\,\psi)dV/V,$$

integrated over the volume of the body.

An elastic field, ϕ, is a field which satisfies the body equations (for the given elastic constants) with no body forces.

Two elastic fields, ϕ, ψ, are said to be *orthogonal* if

$$W(\phi\,.\,\psi)=2\int E(\phi\,.\,\psi)dV/V=0.$$

[*] Prescott, p. 27.

[†] Prescott, p. 188.

We can proceed as before to consider *normal* and *complete* sets of elastic fields.

If ψ is an elastic field it can be proved by a form of Green's theorem, called Betti's theorem, that

$$\mathrm{VW}(\phi \,.\, \psi)=\int \phi'' \,.\, \psi' \, d\mathrm{V}=\int_{\mathrm{B}} \phi \,.\, (\psi')_n \, d\mathrm{S},$$

where the last integral is taken over the bounding surface of the body.

Centrifugal Force.

Let us consider, in particular, the problem of an elastic body rotating uniformly about a fixed axis under no forces except the centrifugal force. Let the z-axis be taken on the axis of rotation and let r be the distance from this axis. Choose

$$u_0=xr^2/8(m+n), \quad v_0=yr^2/8(m+n), \quad w_0=0.$$

Then

$$\begin{aligned}
\mathrm{P}_1&=[(2m+n)x^2+(2m-n)y^2]/4(m+n)=\pi_1,\\
\mathrm{P}_2&=[(2m-n)x^2+(2m+n)y^2]/4(m+n)=\pi_2,\\
\mathrm{P}_3&=(m-n)(x^2+y^2)/2(m+n)=\pi_3,\\
\mathrm{S}_1&=\mathrm{S}_2=0, \quad \mathrm{S}_3=nxy/2(m+n)=\sigma.
\end{aligned}$$

Let ω be the angular velocity of rotation, U, V, W the actual displacements, and put

$$\mathrm{U}=\rho\omega^2(u-u_0), \text{ etc.}$$

In this case $\phi=(u, v, w)$ is actually an "elastic field," that is, a field due to no body forces. On the surface

$$(\phi')_n=(\lambda\pi_1+\mu\sigma, \quad \lambda\sigma+\mu\pi_2, \nu\pi_3),$$

so that $(\phi')_n$ is determinate on the surface.

If $\phi_1, \phi_2, \ldots$ is a complete normal set of elastic fields and if

$$c_r\int_{\mathrm{B}}\phi_r \,.\, (\phi')_n \, d\mathrm{S}/\mathrm{V}=\int_{\mathrm{B}}\phi_r \,.\, (\phi_0')_n \, d\mathrm{S}/\mathrm{V},$$

the required solution is given by

$$\phi=c_1\phi_1+c_2\phi_2+\ldots$$

If the system is completely balanced without the addition of further forces and couples,

$$\int xz \, d\mathrm{V}=\int yz \, d\mathrm{V}=0,$$

and we can choose the x and y axes so that

$$\int xy \, d\mathrm{V}=0.$$

In this case there will be six independent "fields" which are linear in x, y, z (corresponding to constant strain tensors).

Take

$$f_1=(0,z,y),\quad f_2=(z,0,x),\quad f_3=(y,x,0),$$
$$f_4=(x,y,z),\quad f_5=(x,-y,0),\quad f_6=(x,y,-2z).$$

These fields will be orthogonal to one another and the first six normal fields will be

$$\phi_1=f_1/2\sqrt{n},\quad \phi_2=\text{etc.},$$
$$\phi_4=f_4/\sqrt{(9m-3n)},$$
$$\phi_5=f_5/2\sqrt{n},\quad \phi_6=f_6/2\sqrt{(3n)}.$$

Of independent fields of the second degree there will be fifteen, but we shall leave their determination to a later paper. The normal set obtained by proceeding to the third and higher degrees will be applicable not only to the problem of rotating bodies but to the general statical elastic problem in three dimensions.

The University,
Sheffield.

XIX. *Interatomic Distances in Crystals.*
By Prof. W. L. Bragg, *M.A.*, *F.R.S.**

1. In a paper in this Magazine, the author in 1920 (4) gave figures for the radii of atoms deduced from their arrangement in crystals. It was shown that in many cases the distance between neighbouring atoms in a crystal corresponded closely with the sum of the constants for the two atoms concerned, and it was proposed to use this empirical relationship as an aid to X-ray analysis.

Since this paper appeared, other investigators have treated the same problem in a much more fundamental way, and have used data which were not available at the time the original paper was published. The author is in agreement with their more satisfactory treatment of the problem, and has adopted their point of view. Since the figures of the 1920 paper have recently been quoted in several instances, it appears desirable to publish the present note.

2. The examination of a large number of crystal structures has provided a wealth of data on interatomic distances in

---

* Communicated by the Author.

solid bodies. Two ways in which these data may be employed are relevant to the present discussion.

On the one hand, the observed distances may be interpreted by expressions for the mutual potential energy of two atoms in close proximity. From these expressions the condition for the equilibrium of the forces between atom and atom in the crystal may be formulated. This is, of course, the most fundamental way of treating the problem, and must finally supersede other methods. The classical instance of its application is Born's treatment (5) of the alkaline halides and other simple salts. Recently Lennard-Jones (18) has published a most interesting series of papers in which he has linked up the forces between atom and atom in the inert gases, and the corresponding forces in simple crystalline structures composed of ions of similar electronic configuration to the inert gases.

On the other hand, we may make use of empirical relationships which have been found to hold with a very fair degree of accuracy for interatomic distances in crystals. The existence of these relationships is probably due to the rapid increase of the repulsive force between two ions as the distance between them diminishes [*]. This makes it possible, without taking account of the very complicated interaction of forces in a crystal of a complex type, to form an estimate of the distance between neighbouring atoms which is sufficiently accurate for the first stages in the analysis of the structure. Although the exact distance between two neighbouring atoms will depend on the way in which all the surrounding atoms are arranged, as well as on the particular pair under consideration, yet the distance remains approximately constant for a given pair from crystal to crystal. The empirical rules enable one to estimate the point at which the repulsive forces will be of the right order to balance the forces of attraction tending to compress the crystal structure.

This is the assumption which is made when "spheres of influence" are assigned to the ions, and when the atoms are regarded as being elastic bodies packed together and supported by their neighbours. Any given set of figures will only hold for a series of crystals in which there is the same type of chemical bond between the atoms, but this restriction also applies to any calculations based on expressions for mutual potential energy.

---

[*] For instance, the compressibilities of the alkaline halides indicate that the force would be doubled by a decrease in interatomic distance of 7 per cent., if the extrapolation can be carried so far.

In analysing a complex crystal, an estimate of the probable distance between any pair of neighbouring atoms is of the greatest assistance. The positions of the atoms in the crystal are determined by a number of parameters, and the difficulty of analysis increases with this number. Structures with two or three parameters can be attacked in a straightforward manner, all possible values of the parameters being considered and those discarded which do not conform to the observed intensities of X-ray diffraction. As the number of parameters increases, this process becomes so laborious that any method of shortening it is of value. Knowledge of the quantitative laws governing X-ray diffraction is rapidly increasing, and in the author's opinion a point has been reached where reliance may be placed on solutions of crystal structure containing a large number of parameters, when it can be shown that these solutions explain in a satisfactory manner the intensity of the observed reflexions. Many reflexions can be measured in order to check the results, so that there is no lack of equations which must be satisfied by the variable parameters. The difficulty of analysis is similar to that of solving a number of simultaneous equations, and this difficulty is greatly reduced if approximate values of the parameters can be obtained in a simple manner, or certain ranges of their values excluded from consideration as being highly improbable. Empirical rules based on crystals already analysed are of value for this purpose and may be used legitimately. It is not intended to suggest that a structure based on these can be regarded as satisfactorily solved. The final test of the solution must consist in a proof that the proposed atomic arrangement explains the X-ray data, and that no alternative arrangement will do so.

Any attempt to assign radii, or spherical domains, to the ions must be an unsatisfactory compromise, for one is not dealing with definite physical quantities. It must, of course, be recognized that analysis of the functions defining the forces between atoms, such as Lennard-Jones has carried out, supersedes the cruder conception of a certain space occupied by each atom to the exclusion of other atoms. At the same time, the importance of this latter conception in X-ray analysis must not be disregarded. It will probably be true for some time yet that the crystal structures which can be made to yield to X-ray analysis surpass in complexity those to which mathematical analysis can conveniently be applied. Quite approximate estimates of interatomic distance may be used as the first step towards analysis, and it must be counted a fortunate result of the nature of atomic fields that the conception of atoms occupying a characteristic amount of space in the crystal structure to the exclusion of others gives results in a very fair agreement with observation. This conception can be immediately used, however complex the structure, whereas an application of known force-constants can hardly be made until the structure is at any rate approximately determined.

4. A list of atomic or ionic radii has, therefore, as its sole justification its convenience as a means of summarizing observed distances, and of making possible a first approximation to the relative positions of atoms in a structure which is under investigation. Limiting consideration in the first place to cases where the bonds are of the polar type, in the generally accepted meaning of the term, there are, broadly speaking, two sets of ionic radii wdich have been proposed. Both are based on the undoubted fact that interatomic distances are additive in many series of compounds. They differ in that the one set (proposed by the author in 1920, and Niggli⁽⁶⁾ in 1921) assigned values of the radii to the cations which were larger than those of the other set (proposed by Wasastjerna ⁽¹²⁾ in 1923, and foreshadowed by Landé⁽¹⁾ in 1920) by a constant amount of about 0·7 Å. All the anions in the first set are correspondingly smaller by the same amount.

The second set correspond much more closely with the physical reality, in so far as such an arbitrary idea as that of ionic radius can correspond with reality. The author believes that they are preferable for this reason. Both sets give the same estimate of the point at which the repulsion between cation and anion sets in, but the second set also gives an estimate of the point at which the repulsion between anions sets in. Now in actual crystal structures it is often found that in certain directions anions are nearest neighbours. In these cases (where a non-polar bond between the atoms is absent) the author's figures give far too small an estimate of the distance between the anions, whereas Wasastjerna's figures correspond satisfactorily with the observed value.

Wasastjerna's figures were proposed with a clear recognition of their fictitious nature, and with a preliminary discussion of the atomic force-fields which determine interatomic distances. They are given below as ionic radii in Ångström units.

TABLE I.

O^{--} 1·32	F^- 1·33	Na^+ 1·01	Mg^{++} 0·75
S^{--} 1·69	Cl^- 1·72	K^+ 1·30	Ca^{++} 1·02
S^{--} ?	Br^- 1·92	Rb^+ 1·50	Si^{++} 1·20
Te^{--} ?	I^- 2·19	Cs^+ 1·75	Ba^{++} 1·40

This list may be extended to a number of other ions. NH_4^+ and Tl^+ replace Rb^+ with very small alteration in interatomic distance. Pb^{++} replaces in a similar manner Sr^{++}. Be^{++} and Al^{+++} are so small that interatomic distances are generally determined by the mutual repulsion of atoms surrounding them, rather than by repulsion between these metals and the neighbouring anions. In this sense the ions Be^{++} and Al^{+++} may be regarded as fitting into the spaces between the surrounding atoms. Fe^{++}, Co^{++}, Ni^{++}, Zn^{++} are nearly equivalent to Mg^{++}.

Though this set of figures does not apply to atoms united by non-polar bonds, it may be extended to more complex acid radicals such as CO_3^{--}, NO_3^-, ClO_4^-, SO_4^{--}, $SiO_4^{==}$. In every crystal that has so far been analysed, the oxygen atoms in these acid radicals are grouped in a symmetrical way, at the corners of an approximately equilateral triangle in CO_3^{--} and NO_3^-, and at the corners of an approximately regular tetrahedron in ClO_4^-, SO_4^{--}, $SiO_4^{==}$. The distances between oxygen atoms are as follows :—

CO_3^{--}, NO_3^-	2·25 Å. ($CaCO_3$, $NaNO_3$).
SO_4^{--}, ClO_4^-.........	2·45 Å. ($CaSO_4$, $BaSO_4$, $LiKSO_4$, $RbClO_4$).
$SiO_4^{==}$	2·55 Å.–2·7 Å. (Mg_2SiO_4).
	2·7 Å.–2·85 Å. ($Ca_3Al_2Si_3O_{12}$).

These distances between oxygen atoms show wide variations from group to group as might be expected. However, the distance between an oxygen atom of a group, and a neighbouring cation or anion, is given quite satisfactorily by the additive law. A model of the structure may be made by representing the oxygen atoms centred at the points given by the above dimensions, and having radii of about 1·35 Å.

The author* has modified the atomic radii which he originally proposed for purposes of analysis in the way suggested by Wasastjerna. It is very striking, in working

---

[*] W. L. Bragg, Address to the Franklin Institute, Sept. 1924; Solvay Conference (Chemistry) Brussels, April 1925; Royal Institution Discourse, May 1925.

out a new structure, to observe how closely the first approximation obtained by packing together an assemblage with the dimensions of the atomic domains, corresponds with the final structure attained by a careful consideration of the intensities of reflexion. One cannot help being convinced that the idea is useful, and gives a helpful conception of the reasons for the stability of the structure.

Small alterations in Wasastjerna's figures might perhaps be made in order to get a better general correspondence with observed distances, but their approximate nature makes this hardly worth doing.

A very large number of papers on atomic radii have been published, of which only a few are mentioned below. In 1920, Landé (6), in a paper on "The Sizes of Atoms," showed that the interatomic distances in the alkaline halides were approximately additive. Starting with the assumption that in lithium iodide the size of the structure is determined by the repulsions between the iodine atoms, he obtained a set of values for the apparent sizes of the monovalent ions with which Wasastjerna's values are in agreement. Fajans and Herzfeld (3) in 1920 pointed out that the additive law was approximate, and investigated types of fields of force which would explain the observed distances. A very careful review of the molecular volumes of the alkaline halides by Spangenberg (14) showed a regular deviation from an additive law of interatomic distance even in this simple series compounds. A paper by Grimm (8) gives a very complete summary of the relative dimensions of simple and complex ions, as shown by the comparison of isomorphous com-of pounds. Davey (7) made a series of measurements of the alkaline halides, and showed how closely they obeyed an additive law. He proposed a set of atomic radii, based on assigning equal values to K^+ and Cl^-, Rb^+ and Br^-, etc. Everything would point, however, to a structure on a larger scale for the anion than for the corresponding cation. Wyckoff (13), in a paper "On the Hypothesis of Constant Atomic Radii," confirmed the application of the additive law to simple salts, while drawing attention to the many discrepancies which appear if it is applied to elements and compounds of all types. Starting from a different point, he obtained a set of figures corresponding closely to those published by the author. Pease (10) discussed the interatomic distances in diamond-type crystals, and showed that by themselves they formed a consistent series.

5. Wasastjerna, in his paper "On the Radii of Ions," quotes

instances where the set of figures he proposes explains structures in which anions are nearest neighbours. One of these is the structure of lithium iodide, which has already been mentioned in referring to Landé's paper. Another is the structure of $Mg(OH)_2$ and $Mn(OH)_2$, analysed by Aminoff. The author's figures, in assigning a small size to the oxygen, leave a large amount of space to be occupied by the hydrogen atom. The structure should rather be regarded, according to Wasastjerna, as a set of ions $(OH)^-$ in a near approach to hexagonal close-packing, with much smaller positive ions in the interstices.

We may add some other instances. The crystals CdI_2 (11), ZrS_2, $ZrSe_2$ (17), have a structure similar to that of $Mg(OH)_2$, the anions being much larger than the cations. In SnI_4 (15)(16), the iodine atoms are nearly in close-packing. Dickinson remarks that the distance between iodine atoms is about 4·21 Å, as it is in CdI_2, this value being much greater than that deduced from the author's atomic radii. Wasastjerna's figures give estimates for the distances between anions in all these cases which are in agreement with observation.

G. B. Brown and the author (19) have recently drawn attention to some crystals where the distance between oxygen ions is nearly constant throughout the structure, and has an average value of 2·7 Å. In BeO, Al_2O_3, $BeAl_2O_4$, the oxygen atoms are in a close approximation to hexagonal close-packing, and the dimensions of the assemblage are very nearly the same in each case. To illustrate this, we may imagine a rectangular cell containing sixteen points of the hexagonal close-packed assemblage, at a distance apart of 2·7 Å., to be referred to orthohexagonal axes. This is done in order to facilitate the comparison with chrysoberyl, $BeAl_2O_4$, which has orthorhombic symmetry. In the table, the dimensions of this cell are compared with cells containing sixteen oxygen atoms for BeO, Al_2O_3, and $BeAl_2O_4$.

TABLE II.

	a.	*b.*	*c.*
Close-packed assemblage	4·41	9·35	5·40
BeO	4·38	9·32	5·38
Al_2O_3	4·32	9·50	5·48
$BeAl_2O_4$	4·42	9·39	5·47

A paper by G. Menzer (21) has recently appeared on the structure of garnet, $Ca_3Al_2Si_3O_{12}$. In this paper Menzer quotes the author's figures for atomic radii and compares them with the interatomic distances in the structure he suggests, finding in most cases a fair agreement. The author would prefer, however, an interpretation of the structure on rather different lines, laying stress on the distance between neighbouring oxygen atoms. Menzer's figures are as follows:—

	Observed.	Sum of "Atomic Radii."
Si–O..................	1·71 Å.	1·82 Å.
Ca–O	2·31 Å.	2·35 Å.
Al–O	1·95 Å.	2·00 Å.

If the author has interpreted Menzer's structure correctly, each oxygen atom has, as nearest neighbours, a calcium atom and eight other oxygen atoms. The distance Ca—O is significant, as the calcium ion is too large to be packed between oxygen ions. In the rest of the structure the Si and Al atoms fit into the spaces between the oxygen atoms, so that we would expect the latter to be at an average distance of about 2·7 Å. apart. The actual distances between an oxygen atom and its eight oxygen neighbours are, in ngström units, 2·68, 2·68, 2·79, 2·79, 2·85, 2·85, 2·70, 2·84. This both supports the estimate of 2·7 Å. as the distance at which the repulsion between the two ions O^{--} assumes a large value, and is a striking confirmation of the accuracy of Menzer's analysis.

6. The author's paper in 1920 has been criticized as an attempt to prove that atoms under all circumstance occupied an absolute rigid spherical domain, though this interpretation was guarded against by the statement "This additive law is only intended to be regarded as a working approximation, an aid to the analysis of complex structures." Cases which did not correspond with the additive law were quoted, and it was also pointed out that the "atomic radii" did not correspond with the relative dimensions of the atomic structures. The correspondence was deliberately sacrificed in order to obtain a set of figures which held for both polar and non-polar bonds. The analyses of structures which have since been made have shown that this cannot be realized.

In examining crystal structures, however, it is difficult to avoid the impression that the representation of the repulsive forces by a simple inverse power of the interatomic distance is as much a compromise as the conception of atomic domains. The actual law of force is probably much more complex. The repulsion may be taking place between those parts of the atomic structure which approximate most closely, so that a mathematical expression for the force which tended to an infinitely high value for a finite distance between atomic centres might be closer to the truth and hold over a wider range than an inverse power of the distance. The close approximation to an additive law may receive its explanation along these lines.

The discussion of the nature of the repulsive force is beyond the scope of the present note, which is an attempt to show that the conception of atomic domains can render very useful service in crystal analysis, when due care is used in its application and its limitations are recognized.

List of References.

(1) Landé, *Zeitschr. für Physik*, i. p. 191 (1920).
(2) Fajans & Grimm, *Zeitschr. für Physik*, ii. p. 299 (1920).
(3) Fajans & Herzfeld, *Zeitschr. für Physik*, ii. p. 309 (1920).
(4) W. L. Bragg, Phil. Mag. (6) xl. p. 169 (1920).
(5) Born, 'Atomtheorie der festen Zustandes.'
(6) Niggli, *Zeitschr. für Kristallogr.* lvi. p. 167 (1921).
(7) Davey, Phys. Rev. xviii. 2, p. 102 (1921).
(8) Grimm, *Zeitschr. für Phys. Chem.* xviii. 4. p. 353 (1921).
(9) Rinne, *Zeitschr. für Phys. Chem.* c. p. 408 (1922).
(10) Pease, Jour. Amer. Chem. Soc. xiv. 4. p. 769 (1922).
(11) Bozorth, Journ. Amer. Chem. Soc. xliv. 10. p. 2232 (1922).
(12) Wasastjerna, *Soc. Scient. Fenn. Comm. Phys. Math.* xxxv i p. 1 (1923).
(13) Wyckoff, Proc. Nat. Acad. Sci. ix. p. 33 (1923).
(14) Spangenberg, *Zeitschr. für Kristallogr.* lvii. 5. p. 494 (1923).
(15) Dickinson, Jour. Amer. Chem. Soc. xlv. 4. p. 958 (1923).
(16) Mark & Weissenberg, *Zeitschr. für Physik*, xvi. 1. p. 1 (1923).
(17) Van Arkel, *Physica*, iv. p. 286 (1924).
(18) Lennard-Jones, Roy. Soc. Proc. A. cvi. pp. 441, 463, 709 (1924); cvii. pp. 157, 636 (1924); cix. pp. 476, 584 (1925).
(19) Bragg & Brown, Roy. Soc. Proc. A. cx. p. 34 (1926).
(20) Wasastjerna, *Soc. Scient. Fenn. Comm. Phys. Math.* ii. p. 26 (1926).
(21) Menzer, *Zeitschr. für Kristallogr.* lxiii. ½ (1926).

XX. *The Compton Scattering and the Structure of Radiation.*

By T. L. ECKERSLEY, *M.A.* *

COMPTON †, in discussing the scattering of X-rays by free electrons, has evolved a theory which frankly discards the laws of electromagnetism in favour of purely quantum considerations. In justification, he points out the inability of the classical theory to account for the change in wave-length in the scattered radiation, which experiments have shown undoubtedly occurs when very hard γ- or X-rays are used as the exciting source.

In making this statement he must have been unaware of an investigation by Sir J. J. Thomson ‡, who showed that ions or electrons are set in motion in the direction of propagation of electric waves, so that the scattering is effected by electrons which are moving along with the wave. To a fixed observer the scattered radiation will therefore appear of longer wave-length than that of the exciting source, in agreement with experimental results.

The formula evolved by Sir J. J. Thomson is:

$$c^2-(c-v)^2=\frac{e^2c^2\mathrm{H}^2}{m^2p^2} \quad \text{or} \quad \frac{e^2\mathrm{H}^2\lambda^2}{4\pi^2m^2},$$

where c is the velocity of light, v the average drift produced in the direction of propagation, λ the wave-length, e and m the charge and mass of the electron respectively, and H the magnetic force in the wave-front.

A numerical examination of this formula shows that for wave-length of 0·1 Å. the change of wave-length is infinitesimal unless enormous values of H are involved.

In the following investigation the classical methods are employed, and Sir J. J. Thomson's analysis is extended to take account of the relativity variation of mass.

In accordance with quantum ideas, however, the steady state is calculated neglecting the reaction due to re-radiation or scattering, this process being assumed to take place in a sudden transition from one quantum state to another. The steady state is thus unaffected by re-radiation.

In the classical theory the change of wave-length is a function of the intensity of the incident radiation. If in accordance with the experimental evidence the scattered

---

* Communicated by the Author.

† Phys. Review, xxi. p. 483 (1923).

‡ J. J. Thomson, Phil. Mag. ser. 6, vol. iv. p. 253 (August 1902).

frequency is only a function of the incident frequency, there must be a restriction on the intensity of the incident radiation. The assumption that this is in quanta is insufficient to determine this relation, for this only fixes the total energy $h\nu$ in the quantum, and not the intensity of E, which determines the change of frequency.

In the present theory the relation is provided by quantizing the orbit of the scattering electrons, which is found to be periodic. Such a process is perhaps rather outside the scope of the usual quantum theory, which to my mind merely exhibits the four-dimensional (dynamic) structure of the atom; but the theory must stand by the test of results, and these appear to be in accordance with the experimental evidence.

To accept the process outlined here seems to me to be more logical than to discard, with Compton, the whole structure of the electromagnetic laws, which are undoubtedly valid in the lower frequency ranges.

The method which uses the classical theory to calculate the steady states, and only involves the quantum theory to restrict the possible states (or calculate the arbitrary constants), has the merit of retaining the classical theory as far as possible, and is logically self-consistent if we consider the classical theory as exactly applicable to all periodic or quasi-periodic states of motion, and the quantum theory as a guide to define the possible steady states and the probability of transfer of one state to another.

Before entering into mathematical details of the problem, it may be worth while to attempt to give a mental picture of the physical processes which result in the production of a drift of electrons in the direction of propagation, according to the classical theory. Thus an isolated electron in the field of a plane electromagnetic wave will, under the influence of the electric force, in the first place, execute a vibration to and fro along the lines of electric force, *i. e.* at right angles to the direction of propagation of the waves. But in doing so it cuts across the lines of magnetic force H in the wave-front, and is given a resultant forward impulse. It will be found that the mean force is zero when averaged over a large number of periods, so that there is no resultant acceleration, and the average velocity given in the first impulse remains unaltered.

This average velocity v is a function of the frequency and intensity of the incident radiation, and $\frac{v}{c}$ measures the change of frequency of the scattered radiation.

To state the problem explicitly, let us suppose a plane wave:

$$E = E_0 \sin p(t-x/c), \quad t > x/c, \quad E = 0 \text{ for } t < x/c,$$
$$H = H_0 \sin p(t-x/c), \quad ,, \quad H = 0 \quad ,,$$

moving from left to right along the x axis to meet a stationary electron at $x=0$, $y=0$, and $z=0$.

Let the electric force be in the z direction and the magnetic force in the y direction.

The general equations for the movement of the electron are:

$$-m_0\left\{\frac{d^2x_\mu}{ds^2}+\{\alpha\beta,\mu\}\frac{dx_\alpha}{ds}\frac{dx_\beta}{ds}\right\} = F_\nu^\mu J^\nu, \quad . \quad ^*(1.1)$$

where J^ν is the current vector

$$\rho\frac{dx}{dt}, \quad \rho\frac{dy}{dt}, \quad \rho\frac{dz}{dt}, \quad \rho c.$$

F_μ is the tensor

$$\left.\begin{matrix} 0 & -\gamma & \beta & X \\ \gamma & 0 & -\alpha & Y \\ -\beta & \alpha & 0 & Z \\ +X & -Y & -Z & 0 \end{matrix}\right|, \quad . \quad . \quad . \quad . \quad . \quad (1.2)$$

assuming Galilean coordinates.

Also

$$\left.\begin{aligned} \gamma = \alpha &= 0, \\ X = Y &= 0, \\ \{\alpha\beta,\mu\} &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.3)$$

We get the equation:

$$\left.\begin{aligned} m_0\frac{d^2z}{ds^2} &= \rho Z - \rho\beta\frac{dx}{dt}, \\ m_0\frac{d^2x}{ds^2} &= \rho\beta\frac{dz}{dt}, \\ m_0\frac{d^2ct}{ds^2} &= Z\rho v_2. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1.4)$$

---

* Eddington, 'Mathematical Theory of Relativity,' pp. 118, 181.

For our purpose, since β is a function of t, $\beta=\beta_0 e^{ip\left(t-\frac{x}{c}\right)}$, it is best to modify the equation as follows:

$$m_0\frac{d^2x}{ds^2}=m_0\frac{d}{ds}\left(\frac{dt}{ds}\cdot\frac{dx}{dt}\right). \quad . \quad . \quad . \quad . \quad (1.5)$$

Now $m_0\dfrac{dt}{ds}=m$, the value of the mass of the moving electron referred to fixed axes.

$$\frac{d^2x}{ds^2}=\frac{dM_x}{ds}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.6)$$

where M_x is the X component of the momentum of the electron, and

$$\frac{dM_x}{ds}=\frac{dt}{ds}\cdot\frac{dM_x}{dt}; \quad . \quad . \quad . \quad . \quad . \quad (1.7)$$

so that

$$\left.\begin{aligned}\frac{dM_z}{dt}&=\rho\frac{ds}{dt}\cdot Z-\rho\frac{ds}{dt}\cdot\frac{dx}{dt}\cdot\beta,\\ \frac{dM_x}{dt}&=\rho\frac{ds}{dt}\cdot\frac{dz}{dt}\cdot\beta,\\ \frac{dmc}{dt}&=Z\rho\frac{ds}{dt}\cdot\frac{dz}{dt}.\end{aligned}\right\} \quad . \quad . \quad . \quad (1.8)$$

Now $\rho\dfrac{ds}{dt}=$ invariant charge e, so that

$$\left.\begin{aligned}\frac{dM_z}{dt}&=eZ-e\beta v_x,\\ \frac{dM_x}{dt}&=e\beta v_z,\\ \frac{dme}{dt}&=Zev_z,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.9)$$

or, expressing everything in terms of the four vectors M_x, M_y, M_z, mc,

$$\left.\begin{aligned}\frac{dM_z}{dt}&=eZ-\frac{e\beta}{m}\cdot M_x,\\ \frac{dM_x}{dt}&=\frac{e\beta}{m}M_z,\\ m\frac{dme}{dt}&=Zev_z.\end{aligned}\right\} \quad . \quad . \quad . \quad (1.10)$$

If we use units for which E and H are of the same dimensions (as a matter of convenience), the equations are obviously :

$$\left.\begin{aligned} \frac{dM_z}{dt} &= eZ-\frac{e\beta}{mc}M_x, \\ \frac{dM_x}{dt} &= \frac{e\beta}{mc}M_x, \\ m\frac{dmc}{dt} &= ZeM_x, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1.11)$$

the last being the activity equation.

§ 2. We have

$$M_z = \frac{mc}{e\beta}\cdot\frac{dM_x}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.1)$$

and

$$\frac{dM_z}{dt} = \frac{d}{dt}\frac{mc}{e\beta}\frac{dM_x}{dt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.2)$$

Substituting in (1·9) for $\frac{dM_z}{dt}$, we get

$$\frac{d}{dt}\frac{mc}{e\beta}\frac{dM_x}{dt} = eZ-\frac{c\beta}{me}M_x. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.3)$$

Multiplying both sides by $\frac{mc}{e\beta}\frac{dM_x}{dt}$, and denoting this quantity by U, we get

$$U\frac{dU}{dt} = \frac{Zmc}{\beta}\frac{dM_x}{dt} - M_x\frac{dM_x}{dt}, \quad . \quad . \quad (2.4)$$

$$\frac{1}{2}\frac{dU^2}{dt} = \frac{Zme}{\beta}\frac{dM_x}{dt} - \frac{1}{2}\frac{dM_x}{dt}, \quad . \quad . \quad (2.5)$$

or

$$\frac{1}{2}\frac{d}{dt}(U^2+M_x^2) = mc\frac{dM_x}{dt}, \text{ since } Z=\beta. \quad . \quad . \quad (2.6)$$

If we could consider m to be constant, we could get an approximate integral by integrating through with respect to t, but we can proceed more accurately as follows :—

The quantity

$$M_x, \ M_y, \ M_z, \ -mc \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.7)$$

is a four-vector, and the invariant

$$M_x^2+M_y^2+M_z^2-m^2c^2 = -m^2.c^2 \quad . \quad . \quad . \quad (2.8)$$

in the special case of relativity. In this case, $M_y=0$,

$$M_x^2+M_z^2-m^2c^2 = -m^2.c^2, \quad . \quad . \quad . \quad . \quad (2.9)$$

or differentiating,

$$\frac{d}{dt}(\mathrm{M}_x^2+\mathrm{M}_z^2)=\frac{d}{dt}m^2c^2 \quad . \quad . \quad . \quad . \quad (2.10)$$

Now the energy equation derived from 1 and 2 gives

$$\frac{d}{dt}\left(\frac{\mathrm{M}_x^2+\mathrm{M}_z^2}{2}\right)=e\mathrm{ZM}_z. \quad . \quad . \quad . \quad . \quad (2.11)$$

Now

$$m\frac{d\mathrm{M}_x}{dt}=\frac{dm\mathrm{M}_x}{dt}-\mathrm{M}_x\frac{dm}{dt} \quad . \quad (2.12)$$

and

$$\mathrm{M}_x\frac{dm}{dt}=\frac{\mathrm{M}_x}{m}\frac{d}{dt}\frac{m^2}{2}=\frac{\mathrm{M}_x}{m}\frac{d}{dt}(\mathrm{M}_x^2+\mathrm{M}_z^2), \quad (2.13)$$

$$=\frac{\mathrm{M}_x}{m}\frac{e\mathrm{Z}}{c^2}\mathrm{M}_z. \quad . \quad . \quad (2.14)$$

Substituting for M_z from (2.1),

$$\mathrm{M}_x\frac{dm}{dt}=\frac{\mathrm{M}_x}{m}\cdot\frac{e\mathrm{Z}}{c^2}\frac{mc}{c\beta}\frac{d\mathrm{M}_x}{dt}=\frac{\mathrm{M}_x}{c}\frac{d\mathrm{M}_x}{dt}; \quad (2.15)$$

so

$$cm\frac{d\mathrm{M}_x}{dt}=\frac{d}{dt}\left(cm\mathrm{M}_x-\frac{\mathrm{M}_x^2}{2}\right). \quad . \quad . \quad . \quad . \quad (2.16)$$

We have therefore expressed the right-hand side of (a) as a perfect differential with respect to t, which we may write now as

$$\tfrac{1}{2}\mathrm{U}^2=cm\mathrm{M}_x-\mathrm{M}_x^2+c, \quad . \quad . \quad . \quad . \quad (2.17)$$

where c is a constant.

A result which is useful is contained in equation (2.15), *i. e.*:

$$\mathrm{M}_x\frac{dm}{dt}=\frac{\mathrm{M}_x}{c}\frac{d\mathrm{M}_x}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.18)$$

or

$$m=m_0+\frac{\mathrm{M}_x}{c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.20)$$

It is to be remarked that U in our equation (2.4),

$$\mathrm{U}=\frac{mc}{e\beta}\frac{d\mathrm{M}_x}{dt}=\mathrm{M}_z, \quad . \quad . \quad . \quad . \quad (2.21)$$

so that 2·4 may be re-written :

$$\tfrac{1}{2}\mathrm{M}_z^2+\mathrm{M}_x^2=cm\mathrm{M}_x+c. \quad . \quad . \quad . \quad (2.22)$$

Now M_x and M_z are zero together (initially), so that the arbitrary constant c must be zero.

We have

$$\frac{1}{2}\left(\frac{mc}{e\beta}\cdot\frac{d\mathrm{M}_x}{dt}\right)^2 = cm\mathrm{M}_x-\mathrm{M}_x^2 \quad . \quad . \quad . \quad . \quad . \qquad (2.23)$$

or

$$\left(\frac{d\mathrm{M}_x}{dt}\right)^2 = \frac{2e^2\beta^2}{c^2}\left\{\frac{c\mathrm{M}_x}{m}-\frac{\mathrm{M}_x^2}{m^2}\right\} \quad . \quad . \qquad (2.24)$$

Now

$$\frac{\mathrm{M}_x}{m} = v_x = \frac{\mathrm{M}_x}{m_0+\frac{\mathrm{M}_x}{c}};$$

so that

$$\mathrm{M}_x = \frac{m_0 v_x}{(1-v_{x/c})} \quad \text{and} \quad m = \frac{m_0}{1-v_{x/c}}. \quad . \quad . \quad . \qquad (2.25)$$

We therefore get

$$\frac{d}{dt}\frac{m_0 v_x}{1-v_{x/c}} = \frac{\sqrt{2}e\beta}{c}\{cv_x-v_x^2\}^{1/2}, \qquad (2.26)$$

$$\frac{1}{\{cv_x-v_x^2\}^{1/2}}\frac{d}{dt}\frac{m_0 v_x}{(1-v_{x/c})} = \frac{\sqrt{2}e\beta}{c}. \quad . \quad . \quad . \quad . \quad . \qquad (2.27)$$

Now

$$\beta = \beta_0 e^{ip(t-x/c)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2.28)$$

and

$$\frac{d\beta}{dt} = \beta_0 e^{ip(t-x/c)}\,ip(1-v_{x/c})$$

so that since x is a function of t; . (2.29)

$$\frac{1}{(v_{x/c})^{\frac{1}{2}}(1-v_{x/c})^{\frac{1}{2}}}\frac{d}{dt}\frac{v_{x/c}}{(1-v_{x/c})} = \frac{\sqrt{2}e\beta}{cip(1-v_{x/c})}\frac{d\beta}{dt}, \qquad (2.30)$$

or

$$\frac{(1-v_{x/c})^{\frac{1}{2}}}{(v_{x/c})^{\frac{1}{2}}}\frac{d}{dt}\frac{v_{x/c}}{(1-v_{x/c})} = \frac{\sqrt{2}e\beta}{m_0cip}\cdot\frac{d\beta}{dt}; \quad . \quad . \qquad (2.31)$$

and integrating,

$$\left(\frac{v_{x/c}}{1-v_{x/c}}\right)^{\frac{1}{2}} = \frac{e\beta}{\sqrt{2}m_0cip}\beta. \quad . \quad . \qquad (2.32)$$

Taking real parts,

$$\left.\begin{aligned}\left(\frac{v_{x/c}}{1-v_{x/c}}\right)^{\frac{1}{2}} &= \frac{e\beta}{\sqrt{2}m_0cp}\cdot\sin\left(p(t-x/c)\right),\\ \left(\frac{v_{x/c}}{1-v_{x/c}}\right) &= \frac{e^2\beta^2}{2m_0^2c^2p^2}\sin^2 p(t-x/c).\end{aligned}\right\} \quad . \quad . \qquad (2.33)$$

§(3) In this process we have made no mention of the type of wave-train involved. In any case we must suppose the electromagnetic disturbance to be zero until $t=0$ (at $x=0$).

The subsequent history of the wave-train, *i. e.* whether finite or extending to infinity, can only be conjectured.

If it is to be considered as a quantum of radiation, no doubt it is finite. The actual circumstances of the motion of the electron depend to a certain extent upon our choice of the type of wave-train, in particular upon whether the wave-front is a surface of discontinuity or not. At the outset let us take the simplest case, and suppose that the disturbance at $x=0$ is zero for negative values of $t-x/c$ and $R.\beta_0 e^{ip(t-x/c)}$ for positive values of $t-x/c$.

Sommerfeld has shown that in this case the integral

$$\beta = \frac{R}{2\pi}\beta_0\int_{-\infty}^{+\infty}\frac{e^{ip(t-x/c)}}{(p-p_1)}dp \quad . \quad . \quad . \quad . \quad (3.1)$$

represents the complete disturbance if the integral is taken along the real axis, except in the neighbourhood of p_2p_1, this point being encircled by a semicircle in the 4th quadrant. With this form of wave-train, Z and β are continuous at the wave-front, although $\frac{\partial\beta}{\partial x}$ and $\frac{\partial Z}{\partial x}$ are not.

The continuity is associated with the fact that the Fourier integral is convergent at $t=x/c$.

The equation (2.32) still holds, even if we use this form, for

$$\beta = \frac{R}{2\pi}\beta_0\int_{-\infty}^{+\infty}\frac{e^{ip(t-x/c)}}{p-p_1}dp \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.2)$$

and

$$\frac{d\beta}{dt} = \frac{R}{2\pi}\beta_0(1 \quad v_{x/c})\int\frac{ip\,dp\,e^{ip(t-x/c)}}{p-p_1}, \quad t-\frac{x}{c}\neq 0, (3.3)$$

and

$$= (1-v_{x/c})\frac{R}{2\pi}\beta ip, \quad t-\frac{x}{c}\neq 0,$$

so long as

$$t-\frac{x}{c}\neq 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.4)$$

As before,

$$\frac{v_{x/c}}{1-v_{x/c}} = \frac{\rho^2\beta^2}{2m_0{}^2c^2p^2}\sin^2(p)(t-x/c). \quad . \quad . \quad (3.5)$$

The more general case where Z and β are discontinuous at the wave-front can be formed by the integral :

$$\beta = \frac{R}{2\pi}\beta_0\int\frac{e^{i\phi}\,e^{ip(t-x/c)}\,p\,dp}{p-p_1}, \quad . \quad . \quad . \quad . \quad . \quad (3.6)$$

which is not convergent at $t-x/c=0$.

This quantity is zero if $t-x/c<0$, and is equal to

$$-R\beta_0 i e^{i\phi} e^{ip(t-x/c)},$$

$$i.e., \quad \beta_0 \sin p(t-x/c+\phi),$$

when $t>x/c$.

Equation (3.5) is now modified by the addition of a constant:

$$\left(\frac{v_{x/c}}{1-v_{x/c}}\right)^{\frac{1}{2}} = \frac{e\beta_0}{\sqrt{2mcp}} \cdot \sin p(t-x/c+\phi) - C, \quad . \quad (3.8)$$

and the constant C must equal $\sin\phi$, so that $v_x=0$ when $t=0$, as required.

Thus

$$\left(\frac{v_{x/c}}{1-v_{x/c}}\right) = \frac{e^2\beta_0^2}{2m_0^2c^2p^2}\{\sin(p(t-x/c)+\phi)-\sin\phi\}^2 \quad (3.9)$$

when the wave-front is discontinuous.

Reverting to our former expression, we can get the complete integral of the motion; *i. e.* the relation between x and t is as follows:—

If we put

$$p(t-x/c) = y, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.10)$$

then

$$\frac{dy}{dt} = p(1-v_{x/c})$$

and

$$\frac{v_{x/c}}{1-v_{x/c}} = \frac{e^2\beta_0^2}{2m_0^2c^2p^2}\sin^2 y = \zeta^2 \sin^2 y, \text{ say}, \quad . \quad (3.11)$$

or

$$pv_{x/c} = \zeta^2 \sin^2 y \frac{dy}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.12)$$

$$\frac{p}{c}\frac{dx}{dt} = \frac{\zeta^2}{2}\frac{d}{dt}\left(y-\frac{\sin 2y}{2}\right); \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.13)$$

and integrating,

$$\frac{px}{c} = \frac{\zeta^2}{2}\left(y-\frac{\sin 2y}{2}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.14)$$

$$\frac{x}{c} = \frac{\zeta^2}{2c}\left(t-\frac{x}{c}\right) - \frac{\zeta^2}{4p}\sin 2p\left(t-\frac{x}{c}\right). \quad . \quad (3.15)$$

No constant of integration is needed, since the condition $x=0$ when $t=0$ is satisfied identically by this relation. We thus have the required relation between x and t.

The corresponding values of v_z and Z may be obtained from (3), *i. e.*:

$$\mathrm{M}_z=\frac{me}{e\beta}\frac{d\mathrm{M}_x}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.16)$$

$$=\frac{me}{e\beta}\frac{\sqrt{2}e\beta}{c}\{cv_x-v_x^2\}^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.17)$$

or

$$v_z=\sqrt{2}c\left(\frac{v_x}{c}\right)^{\frac{1}{2}}\left\{1-\frac{v_x}{c}\right\}^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.18)$$

$$v_z=\sqrt{2}(1-v_{x/c})\frac{(v_{x/c})^{\frac{1}{2}}}{(1-v_{x/c})^{\frac{1}{2}}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.19)$$

Thus

$$v_z=c(1-v_x/c)\frac{e\beta_0}{m_0cp}.\sin(p)(t-x/c)$$

$$=\frac{e\beta_0}{m_0p^2}\sin p(t-x/c)\frac{d}{dt}(t-x/c) \quad . \quad . \quad . \quad (3.20)$$

and

$$z=-\frac{e\beta_0}{m_0p^2}\{\cos p(t-x/c)-1\}$$

$$=-c\frac{\zeta}{p}\sqrt{2}\{\cos p(t-x/c)-1\}, \quad . \quad . \quad . \quad (3.21)$$

since $z=0$ when $t=0$.

§ (4) This forms the conclusion of the calculation of the steady state on the classical theory.

It will be observed that on this basis there is a definite drift of the electron with an average velocity $\frac{1}{4}\frac{e^2\beta_0^2}{m_0^2p^2c^2}$ ($v_{x/c}$ small) in the direction of propagation.

Combined with the periodic v_z motion this gives a scattered wave of a frequency which differs from that of the existing source by the amount $\delta\nu$, where $\frac{\delta\nu}{\nu}=\frac{v_x}{c}(1-\cos\theta)$, the scattering angle θ being the angle made with the positive normal to the wave-front.

In respect of the factor $1-\cos\theta$, the result agrees with that determined experimentally by Compton. The value, however, is a function of the intensity β of the incoming wave. There should therefore be no fixed value of the change of frequency unless there is a restriction on the value of β, occasioned, for instance, by the quantum structure of the incident radiation.

It might be thought sufficient at first sight to postulate the energy of the incident radiation as $h\nu$, where ν is the frequency; but this determines only the total energy, and not the value of β, which determines the energy per unit volume. The procedure which naturally suggests itself is to treat the momentum M_z—which is periodic—according to the rules of the quantum theory, *i. e.* to suppose that the periodic motion of the electron is one of the specially determined steady quantum states.

We should then put

$$\oint M_z\,dz = nh,$$

and the process is more natural in that $\oint M_z\,dz$ expressed as a function of z turns out to be exactly an inverse periodic function, associated with which is the modulus of periodicity obtained by the integration round the two branch points of M_z.

Thus

$$\oint M_z\,dz = \oint \frac{mc}{e\beta}\cdot\frac{dM_z}{dt}\,dz \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4.1)$$

$$= \oint \frac{mc}{e\beta}\,\frac{\sqrt{2}e\beta}{c}(cv_x)^{\frac{1}{2}}(1-v_{x/c})^{\frac{1}{2}}. \quad . \qquad (4.2)$$

Now

$$m = \frac{m_0}{1-v_{x/c}} \quad \text{by} \quad (2.25),$$

$$\oint M_z\,dz = \oint \frac{m_0\sqrt{2}c(v_{x/c})^{\frac{1}{2}}}{(1-v_{x/c})^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \qquad (4.3)$$

$$= \oint \frac{e\beta}{pc}.\sin(p(t-x/c))\,dz. \quad . \quad . \qquad (4.4)$$

Now, by (3.21),

$$\cos p(t-x/c) = \frac{zp}{c\zeta\sqrt{2}}+1 \qquad = z', \text{ say}, \quad . \quad . \quad . \qquad (4.5)$$

$$\sin p(t-x/c) = \sqrt{1-z'^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4.6)$$

$$dz = c\zeta\sqrt{2}\,dz',$$

$$\oint M_z\,dz = \oint \frac{m_0c\zeta\sqrt{2}}{p}\sqrt{1-z'^2}\,dz'c\zeta\sqrt{2} \qquad (4.7)$$

$$= \frac{2m_0c^2\zeta^2}{p}\oint\sqrt{1-z'^2}\,dz$$

$$= \frac{2m_0c^2\zeta^2\pi}{p} = n_1h, \quad . \quad . \quad . \quad . \qquad (4.8)$$

$$\zeta^2 = \frac{n_1h\nu}{m_0c^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4.9)$$

for $n=1$, *i. e.* the 1-quantum state

$$\zeta^2 = \frac{h\nu}{m_0c^2}. \qquad (4.10)$$

A guarantee of the general reasonableness of our choice in the method of quantizing the orbit of the electron is contained in the following relation :—

The total kinetic energy of the electron can be expressed, in accordance with the relativity theory, in the form :

$$(m-m_0)c^2 = \text{KE}. \qquad (4.11)$$

Now

$$m = m_0\frac{1}{1-v_{x/c}}. \qquad (4.12)$$

$$\therefore \quad \text{KE} = m_0c^2\left(\frac{v_{x/c}}{1-v_{x/c}}\right) \qquad (4.13)$$

$$= m_0c^2\zeta^2\sin^2 y$$

$$\cdot\text{KE}_{\text{max.}} = h\nu.$$

Now the energy equation gives

$$c^2m\frac{dm}{dt} = mv_zZe, \qquad (4.14)$$

$$c^2\frac{dm}{dt} = v_zZe, \qquad (4.15)$$

$$\frac{d\text{KE}}{dt} = Ze\frac{dz}{dt}$$

$$\text{or} \quad \frac{d\text{T}+\text{W}}{dt} = 0 \text{ and } \text{T}+\text{W} = h\nu, \qquad (4.16)$$

where

$$\text{T}=\text{KE}+\text{W}= -\int Ze\frac{dz}{dt}\,dt, \qquad (4.17)$$

which is identically satisfied on using the expressions for Z and $\frac{dz}{dt}$ we have found in eq. (3·21)

The orbital energy is $h\nu$. This is in accordance with the ordinary notion of the quantum theory, since the initial state of the electron was one of zero energy level, and $h\nu$ is here given as the difference in energy level of the zero and 1-quantum state.

§ (5) This solution just obtained I would term "The Selected Semi-Classical Solution," to distinguish it from Compton's purely quantum solution. It corresponds exactly to the solutions of the orbital motions of electrons under central forces in the atom.

I call it "selected," as quantum considerations are used in fixing the amplitude of the motions; it is semi-classical because in the equations of motion no account is taken of re-radiation or scattering, which, according to quantum principles, must be considered to be a separate process involving a change from one quantum state to another: this change, involving re-radiation, may be considered to take place when the train of waves has passed over the electron. We are therefore led to consider a second quantum state, and in accordance with the idea presented here, it should, if possible, be one which satisfies the field equations, the passage from the first to the second state being, of course, accompanied by a scattered radiation. The procedure which is perhaps least open to criticism from the quantum point of view, and for which there is strong experimental evidence, is to assume that, at least formally, this final state is the one calculated by Compton. The conservation of energy and momentum are used to calculate the path and velocity of the electron and the direction, intensity, and frequency of the scattered quantum, which is supposed to be a directed quantity.

This process is consistent on the average with the field equations.

The equations which fix this state are:

$$\left.\begin{aligned} \frac{h\nu}{c} &= \frac{h\nu_x{}'}{c} + \mathrm{M}_x, \\ 0 &= h\nu_\rho{}' - \mathrm{M}_\rho, \\ \nu_x{}'^2 + \nu_\rho{}'^2 &= \nu'^2. \end{aligned}\right\} \text{ Momentum Equations, . } \quad (5.1)$$

$$h\nu - h\nu' = (m - m_0)c^2, \quad \text{Energy Equation, . . } \quad (5.2)$$

$$\mathrm{M}_x{}^2 + \mathrm{M}_y{}^2 = (m^2 - m_0{}^2)c^2. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5.3)$$

These equations give rise to the following frequency relation:

$$\frac{\delta\nu}{\nu} = \frac{\chi^2(1 - \cos\theta')}{(1 - \chi^2\cos\theta')}, \quad \text{where } \chi^2 = \frac{\dfrac{h\nu}{m_0c^2}}{1 + \dfrac{h\nu}{m_0c^2}}, \quad . \; . \; . \quad (5\cdot 4)$$

which is approximately

$$\frac{\delta\nu}{\nu} = \frac{h\nu}{m_0c^2}(1 - \cos\theta'), \quad . \; . \; . \; . \; . \; . \quad (5.5)$$

Correspondence.

This method exhibits the change of frequency on scattering as a purely quantum process, involving the idea of frequency as a determinant of the energy according to the relation $W=h\nu$; but it is the purpose of this paper to exhibit this change of frequency as a Doppler effect, in order to bridge over the gap between the Compton theory on one side and the classical theory on the other side, which undoubtedly applies to long-wave phenomena, and to use the idea of selected statical states for this purpose.

In this manner the solution (1) may be considered as a detailed expression of an intermediate state in the Compton analysis, introduced so as to bring this more in line with the usual methods of quantum analysis and to help to bridge over the gap just referred to.

In order to bring in the classical idea of Doppler effect, the following method may be used:—As we have seen, the process of re-radiation must occur in the jump from the first to the second quantum state. Since there is no re-radiation during the passage of the train of waves over the electron, the velocity of drift occasioned does not determine the Doppler change of frequency of the scattered radiation; but this latter must be determined by velocity after the change. By a suitable choice of the conditions at the end of the train we can continue the solution without discontinuity, so as to give an x velocity from which the Doppler effect corresponding to the Compton effect may be deduced.

Thus the x velocity determined from solution (1) is:

$$\frac{v_x}{c}=\frac{\frac{h\nu}{m_0c^2}\sin^2 p\left(t-\frac{x}{c}\right)}{\left\{1+\frac{h\nu}{m_0c^2}\sin^2 p\left(t+\frac{x}{c}\right)\right\}}. \quad . \quad . \quad . \quad (5.6)$$

If the train is chosen to end when

$$\sin p\left(t-\frac{x}{c}\right)=1, \quad . \quad . \quad . \quad . \quad (5.7)$$

the value of $\frac{v_x}{c}$ will be

$$\frac{v_x}{c}=\frac{\frac{h\nu}{m_0c^2}}{1+\frac{h\nu}{m_0c^2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.8)$$

and the corresponding Doppler effect will be

$$\frac{\delta\nu}{\nu} = \frac{v_x}{c}(1-\cos\theta) \bumpeq \frac{h\nu}{m_0c^2}(1-\cos\theta), \quad . \quad . \quad (5.9)$$

which corresponds with the Compton change of frequency.

Or we may arrive at the Doppler effect idea as follows:—

In developing the relation (5.5) from the equations (5.1), (5.2), (5.3) according to Compton's method, we get the relation

$$\mathrm{M}_x = \frac{h\nu}{c}(1-\cos\theta) \text{ approx.}, \quad . \quad . \quad (5.10)$$

or

$$\frac{v_x}{c} = \frac{h\nu}{mc^2}(1-\cos\theta),$$

and the corresponding Doppler effect would be

$$\frac{v_x}{c} = \frac{h\nu}{mc^2}(1-\cos\theta), \quad . \quad . \quad . \quad . \quad (5.11)$$

which is the relation already obtained.

Thus the change of frequency on scattering may either be considered as an effect due to the energy removed from the incident wave by the recoil electron, *i.e.* as a purely quantum energy change, or as a Doppler effect associated with the velocity v_x of recoil.

These two aspects enable one to pass over from the quantum aspect as developed by Compton to the classical aspect, which follows as a result of the application of the ordinary field laws, by the process of building up a statistical state from the individual quantum process, the relative probability of emission in various directions being determined by the field equations. The details of such a process must be left to a future paper.

The results obtained by the method of this paper are formally just the same as those obtained by Compton; but the method outlined here seems to bring relation between the field equation and the quantum processes into a clearer light, and to pave the way to the understanding of the relation between the individual quantum processes on the one hand and the electromagnetic state as calculated from the field laws which apply on the longer waves on the other. The exhibiting of the quantum process as a selected classical solution, and the identification of the quantum and Doppler aspect of the change of frequency, ensures that a proper choice of the statistical aggregate of quantum processes must conform to the ordinary field equations.

It should be noted that the Einstein conception of a quantum of radiation having a definite direction of travel in space is used throughout, and it seems to me that this is a logical necessity if quantum and relativity notions are to be reconciled.

For suppose the quantum were a spherical type wave, such as, for instance, is radiated from a source at O vibrating in a vertical direction, if the frequency were ν, the corresponding energy would be $h\nu$.

Now refer this system to a set of axes moving relatively to source with the velocity v: the various parts of the spherically-radiated quantum will have different frequencies, and the relation $W=h\nu$ will no longer have any meaning.

I have been guided throughout in fixing the quantum rules by the consideration that any quantity which can be defined in the classical theory—for instance, $\delta\nu/\nu=v/c$—should not clash with the quantum definition of $\delta\nu$, *i. e.* the same quantity. In this manner we have been led to a *definite* value of the change of frequency in scattering which has been observed.

It must be admitted, of course, that the work has been carried out with half an eye on the expected result; but the real value lies in the fact that the quantum conditions must be introduced, and these are naturally and inevitably introduced through the only really periodic quantity v_z. In using this we find the orbited energy to be in accordance with the known quantum principles.

We can picture the process outlined here as the arrival of a quantum $h\nu$ of radiation at the stationary electron, an absorption of this energy by the electron, and a consequent transference of this to the 1-quantum state with energy $h\nu$ (fixing the amplitude of oscillation M_z); finally, a transition from the 1-quantum state to the 2-quantum state, with an emission of scattered radiation with frequency and energy determined by the difference of energy level in the 1 and 2 states, *i. e.*,

$$h\nu' = h\nu - \frac{mv_x^2}{2} = W_1 - W_2,$$

each steady state being rigidly defined by the classical theory (of course neglecting the effect of re-radiation). It is then found that the change in frequency on scattering may either be regarded as a change of energy content of the radiation, or as a Doppler effect associated with the recoil velocity v_x, at least to the first approximation.

§ 6. The further consequences of this theory have a bearing on the structure of radiation.

This is rather to be expected, as this example illustrates perhaps the simplest case of interaction between the quantum and the electron.

The quantity ζ^2 has two interpretations. From the quantum point of view it is the ratio of the quantum of energy $h\nu$ to the potential energy of the electron m_0c^2. From the classical point of view it involves β^2, the energy density reckoned in the ordinary manner, thus:

$$\zeta^2 = \frac{h\nu}{m_0c^2} = \frac{e^2\beta^2}{m_0{}^2p^2c^2} \text{ (energy/vol.} = \beta^2 \text{ in our units),}$$

so that the energy density in the incident radiation is determined by the relation:

$$\beta^2 = \frac{m_0p^2h\nu}{e^2} = \frac{4\pi^2m_0h\nu^3}{e^2} \quad . \quad . \quad . \quad . \quad . \quad (6.1)$$

Now we know the total energy in the incident radiation, i.e. $h\nu$; so that if β^2 is supposed to be uniformly distributed in space, the ratio $\frac{h\nu}{\beta^2} = \frac{e^2}{4\pi^2\nu^2m_0}$ should be the volume in which the quantum is contained, and in calculating this we should get an insight into the structure of radiation.

Now the quantity $\frac{e^2}{m_0c^2}$ has the dimensions of a length. In the usual electromagnetic theory it expresses the linear dimensions of the electron, according to the relation:

$$m_0 = \frac{e^2}{6\pi ac^2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.2)$$

$$\therefore \quad \text{Vol.} = \frac{e^2}{4\pi^2\nu^2\frac{e^2}{6\pi ac^2}} = \frac{3ac^2}{2\pi\lambda^2}, \quad . \quad . \quad . \quad . \quad . \quad (6.3)$$

or

$$\text{Vol.} = \frac{3a\lambda^2}{2\pi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.4)$$

where "a" is the radius of the electron.

Also we may put it in the form:

$$\text{Vol.} = \frac{4\pi a^3}{3}\frac{1}{2}\left(\frac{3}{2}\frac{\lambda}{2\pi a}\right)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.5)$$

so that the volume tends to that of an electron when $\lambda = \sqrt{2}\frac{2\pi a}{3}$; *i. e.*, the quantum apparently shrinks to electronic dimensions when the wave-length is of the order of the electronic radius.

A quantum no doubt consists of a finite train of oscillations. We may perhaps be allowed to consider the electron as remaining in the 1-quantum state during the time that this quantum train passes over the electron. Now by combining classical principles with Einstein's probability coefficients—*i. e.* $A_{1\to 2}$, $B_{2\to 1}$—E. A. Milne* has arrived at a formula which expresses the mean duration of a given quantum state. It is

$$\tau = \frac{c}{4\pi^2 a\nu^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.6)$$

an expression which, as has been pointed out, does not involve h and is therefore independent of the atomic structure, and should be applicable to the type of electronic vibration envisaged in this case.

In the present analysis exactly the same result can be obtained by assuming that on the average the re-radiation is what it would have been on the classical theory; thus if τ is the average duration of the quantum state 1, $\frac{h\nu}{\tau}$ will be equal to the rate of radiation calculated on the classical lines. Thus

$$\frac{h\nu}{\tau} = \frac{1}{2}\frac{e^2}{6\pi}\frac{\Gamma^2}{c^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.7)$$

where Γ is the acceleration.

$$\Gamma = \frac{dv_z}{dt} = \frac{d}{dt}\frac{e\beta}{mp}\sin pt \text{ approx.}$$

$$= \frac{e\beta}{m}\cos pt. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.8)$$

The mean rate of radiation of energy is therefore

$$\frac{1}{2}\frac{e^2p^2}{6\pi c^3}\left(\frac{e\beta}{mp}\right)^2,$$

and is independent of p.

---

* Monthly Notices R. A. S. p. 743, No. 8, June 1925.

$$\frac{h\nu}{\tau}=\frac{1}{2}\frac{e^2p^2}{6\pi c}\left(\frac{\beta e}{m_0pc}\right)^2=\frac{e^2p^2h\nu}{6\pi m_0c^3}, \quad . \quad . \quad . \quad (6.9)$$

so that

$$\frac{1}{\tau}=\frac{e^2p^2}{6\pi m_0c^3};$$

and since $m_0=\frac{e^2}{6\pi ac^2}$,

$$\frac{1}{\tau}=\frac{4\pi^2\nu^2a}{c} \text{ as before.} \quad . \quad . \quad . \quad (6.10)$$

But if we are to retain the same mental picture of the process as before, $c\tau$ must represent the length of a train of oscillations.

One curious consequence of this formula is the following:—

The number of oscillations in the train is $\nu\tau$, or $\frac{c}{4\pi^2a\nu}=\frac{\lambda}{4\pi^2a}$. The number of oscillations in a train tends to unity as $\lambda\rightarrow4\pi^2a$. This is in agreement with the fact that the quantum appears to shrink up to the size of an electron for this frequency. The quantum appears to lose its periodic nature at these high frequencies. What the meaning of $h\nu$ in the formula $W=h\nu$ is, very obscure! This result is perhaps only apparent and due to some approximation introduced into the last stage of the calculation, and is only true if $c\tau$ represents the actual length of the train of oscillations.

On this basis, the length of the train of oscillations is $c\tau$. We may now express the volume V in the form :

$$V=\frac{3ac^2}{2\pi\nu^2}=\frac{6a^2c^2}{4\pi^2\nu^2a}=6a^2c\tau. \quad . \quad . \quad . \quad (6.11)$$

From this point of view, the quantum appears to be contained within a cylinder or tube of radius $\sqrt{\frac{6a}{\pi}}$, or practically the electronic radius and length of $c\tau$. It is perhaps as well to note that this volume is not a fixed quantity ; it seems to adjust itself to the radius of the particle acted upon by the quantum. For instance, if the electrified particle had been a proton, the equivalent value of "a" in formula would have been proportionally smaller, and the quantum would have to adjust itself to this smaller radius. These results inevitably suggest the tube of force attached to the electron or proton, the quantum being a disturbance propagated along this tube, as a state of distortion say.

The tube ends in its appropriate electron or proton, and its approximate diameter is correctly given if some latitude is allowed in fixing the structure of the electron or proton.

The motion of the tube must be fixed by the electromagnetic laws. It is well known, for instance, that the second set of circuital equations can be deduced from purely kinematic considerations of the movement of discrete tubes of force, if the magnetic force is interpreted as the velocity of the tube at right angles to itself.

The whole would form a very compelling picture, were it not that the interference effects are still wholly unexplained, and that the nature of the jump from one steady state to another is also physically difficult to picture.

If we take the view that it is the function of theory to provide an accurate mathematical description of the physical facts, the relativity quantum theory outlined here is singularly adequate—not that it is complete, since the framing of the quantum rules has certainly not been achieved yet.

A theory must pass a very strict test nowadays; it must not only be accurate, it must also be a convenient and powerful instrument of thought. It is a commonplace reflexion, for instance, that certain problems are much more easily solved in terms of certain coordinates than others, and that they may take on an aspect of artificial complexity if inconvenient coordinates are chosen. I have been struck throughout the foregoing analysis with the ease with which the solution unfolded itself; and although it would be foolish to take this as a guarantee of correctness, it certainly seems to indicate that it is a simple mode of expression of the realities involved in one of the simplest of quantum processes.

It will be seen that this scheme really differs very little from Compton's theory. The quantum of energy as portrayed by this theory is very similar to the material particle envisaged by Compton in his theory (for frequencies comparable with $\frac{m_0c^2}{h}$), the contraction in volume being a striking example of this similarity. Compton's theory short-circuits the analytical details of this by using the principles of conservation of energy and momentum which are, of course, implicit in the present classical quantum theory. The present method may be perhaps looked upon as strengthening the assumption upon which Compton's theory is based—*i. e.*, that the quantum acts as a particle which exchanges its energy (in accordance with the ordinary laws of momentum and energy exchange) in a collision.

It is perhaps significant, in view of recent speculations concerning the transformation of matter into radiation (for example, at intensely high temperatures in the interior of stars), that at these frequencies, *i.e.* of the order of $\frac{m_0c^2}{h}$, the distinction between the material element, *i.e.* electrons and protons, and the quantum of radiation seems to disappear, for the energy and volume are of the same order; and if we accept the approximate formula for the number of oscillations in a quantum, a relation which, however, seems to me of very doubtful validity, the quantum loses its periodic structure at these frequencies, and there is but little left to distinguish it from a proton or electron, say.

It is hoped that this paper may pave the way to a fuller understanding of the relation between the quantum and classical theories of radiation.

Perhaps too much stress should not be laid on the physical picture of the volume of a quantum as portrayed here; but if we are to retain our present ideas of time and space as extended by Einstein, we must regard this quantity at least as dimensionally a volume.

XXI. *Note on the Molecular Association of Benzoic Acid in Benzene.* By J. A. Wilcken, *B.Sc., Ph.D., Lecturer in Electrical Engineering at Armstrong College, Newcastle-upon-Tyne* [*].

THE question as to the connexion between dielectric and other physical and chemical properties of matter, which has an important bearing on problems of cable insulation, has led to the investigation into the molecular nature of solutions, and as a type, benzoic acid in benzene has been examined.

Auwers [†] and his co-workers, and Beckmann [‡] have dealt with a large number of solutions of this class, but whereas the former attributes the abnormal behaviour (freezing-point depression) to mutual influence of solute and solvent, the latter inclines to the view that complex molecules are formed. Turner [§] leaves the question open.

This part of the work had been temporarily discontinued, but Prof. Partington's and Mr. Rule's valuable contribution to the subject in the May issue of this Journal suggested that the preliminary results here given might be of some interest.

---

[*] Communicated by the Author.

[†] *Zeitschr. Physikal. Chemie,* xii. pp. 689-722 (1893); *ibid.* xxx. pp. 300-340 (1899).

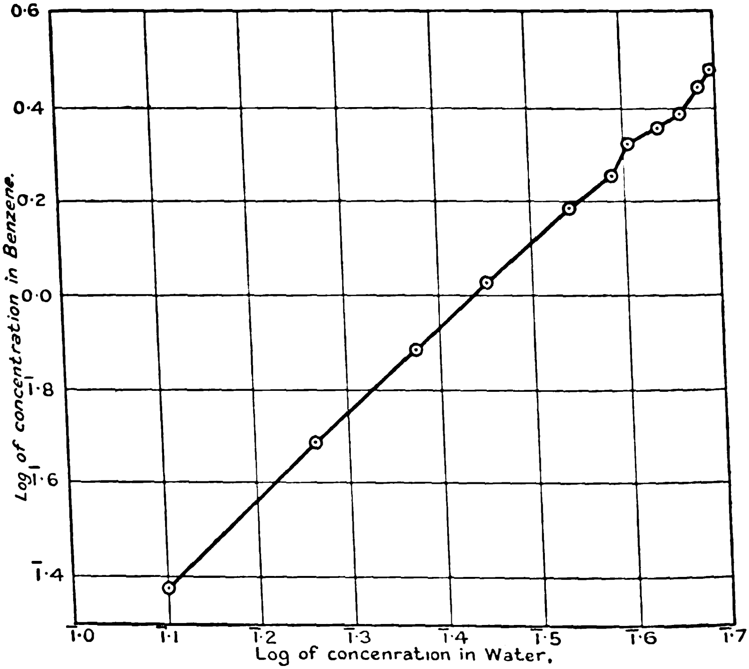
[‡] *Ibid.* xxii. pp. 609-618 (1897).

[§] 'Molecular Association' (Longmans).

Freezing-point determinations carried out with an ordinary Beckmann apparatus gave data too irregular to warrant any conclusive inference, although they seemed to point to a molecular weight swinging between 2½ and 1½ times the normal value.

A series of graded solutions was then prepared, of concentrations varying from 0·040 grm. to 0·564 grm. benzoic acid to 100 grms. benzene, and with these solutions the partition coefficients between pure (conductivity) water and benzene were determined, the titrations being carried out with a standardized baryta solution (ind. phenol-phthalein). The separating funnel was kept carefully at 6°·0 C.

The diagram below shows the relation between the log. of the concentration in benzene and the log. of the corresponding concentration in water. It is seen that the slope of the line deviates appreciably from unity, indicating that the matter is not so simple as the formation of double molecules; the scale of abscissæ is twice that of the ordinates. Might not the process of association pass through a metastable and a labile state, somewhat similar to those of the crystallization of solutions, as found by Miers and Isaac* ?



---

* Journ. Chem. Soc. lxxxix. pp. 413–454 (1906).

XXII. *Further Studies on the Deformation of Tungsten Single Crystals.* By F. S. Goucher. (Communication from the Staff of the Research Laboratories of the General Electric Co., Wembley.) *

[Plates II.-V.]

Summary.

The crystals studied are the large crystals formed in recrystallized hard-drawn pure tungsten wires such as were used in the previous experiments, and in addition Pintsch single crystal wires which can be similarly deformed at lower temperatures.

Measurements on the rate of flow of the pure tungsten crystals under constant load at both 2000° K. and 1000° K. show an internal hardening which increases rapidly in the early stages of deformation and which tends to become proportional to the increase of stress in the later stages; this stage occupies the major portion of the time required for the fracture of such crystals. The hardening is greater at the lower temperature, and there is evidence that the rate of deformation is an important factor in the hardening process. This hardening may be removed by annealing at 2500° K. for 2 minutes.

An X-ray study of these crystals at all stages of their deformation reveals distortions—crystallographic in nature—which increase progressively with the degree of deformation. Annealing these crystals produces no apparent alteration of this distortion. Evidence is obtained that the stress is important in the determination of the degree of distortion. Fractured crystals show the distortion in a very marked degree.

A comparison of the resolving power of crystals deformed at 1000° K. in the hard and in the annealed states shows no measurable difference, whereas Pintsch wires similarly deformed at room temperature show an impaired resolving power which improves on annealing; this is not accompanied by any change in mean reflecting angle exceeding 0·05 per cent.

A microscopic examination of these crystals before and after annealing confirms the persistence of the crystal distortion but shows a pronounced difference in the etching effect which can only be explained by a greater differential rate of etching in the case of the unannealed crystals.

The experiments support the view that hardening is due to residual elastic strains produced by the deformation process rather than the mere fact of crystal break up.

(1) *Introduction.*

A systematic study of the strength of tungsten single crystals taking into account the relation between the rate of deformation on the one hand and the load, temperature, and crystal orientation on the other, has already been described[*]. The measurements were made by taking the time required to fracture fine tungsten wires composed of comparatively large crystals, many of which occupied locally the complete volume of the wire. When such wires were subjected to a constant load at any given temperature, deformation occurred in certain of these large crystals depending on their orientation, and one eventually fractured with the formation of a wedge-shaped structure symmetrically inclined to the stress. This structure was explained by a process of successive small slips parallel to two sets of crystal planes, and the time of fracture was considered as an inverse measure of the mean rate of flow along such planes. No attempt was made, however, to measure any variations in the rate of flow which might occur during the deformation process.

---

* Communicated by the Director.

A subsequent investigation [†] associated the deformation with slip on definite crystallographic planes and in definite crystallographic directions—the (112) planes and the [111] directions—but revealed marked distortions, also of a crystallographic nature. These distortions appeared as bendings of the crystal planes about an axis at right angles to the direction of flow, and were of such a magnitude as to be inconsistent with the preservation of continuity of the crystal lattice as there appeared to be no marked alteration of the lattice parameters. It seemed probable that the hardening effect of deformation was in some way connected with these distortions.

The present experiments were initiated with the object of studying the variations of rate of flow throughout the deformation process as a measure of variations in slip resistance, and at the same time to study the distortions produced by the deformation both from the point of view of the break up of the crystal, and of any possible variations in the lattice parameter, in the hope of throwing further light on the cause of hardening due to deformation.

Some progress in this direction has been made by the study of single crystals of other metals. The facts of crystal hardening independent of changes of orientation, of the crystallographic nature of distortion, and of crystal break up, have now been established. Some workers associate the cause of hardening with very small residual elastic strains as a logical consequence of the distortions, whereas others associate it with the boundary conditions between broken up crystal fragments. The difficulty has been the lack of direct X-ray evidence for the existence of the lattice strains or of experiments directly associating break up with the production of hardness or its removal. Recently van Arkel[*] has shown that broadened diffuse lines which become sharp on annealing may be obtained with hard-drawn fine wires of certain metals such as tungsten and platinum, whereas very soft metals like lead and tin do not show the effect. He ascribes the broadening to a distortion of the crystal lattice, but the fact that it might equally well have been produced by very small crystal fragments—as he himself has pointed out—makes the evidence inconclusive.

---

[*] Phil. Mag. xlviii. p. 229 (Aug. 1924).

[†] Phil. Mag. xlviii. p. 800 (Nov. 1924).

Our experiments have now reached a stage where they are of interest in this connexion, and the following account is therefore given.

(2) *Experimental.*

The test wires were prepared by annealing hard-drawn pure tungsten wires 0·2 mm. in diameter and 10 cm. in length to a temperature of 3100° K. for a period of 2 to 3 minutes, as in the case of the previous experiments. Owing to inter-crystalline brittleness below 900° K. these wires could not be used for deformation at lower temperatures, and in cases where this was required Pintsch single crystal wires were used. Pintsch wires contain about 2 per cent. of thorium oxide, and a description of their preparation may be found elsewhere[†].

The methods employed for the heat treatment and deformation of these test wires were essentially the same as those used previously, the wires being heated electrically in a vacuum and the tension being applied by means of a tungsten and steel buoy floated in mercury.

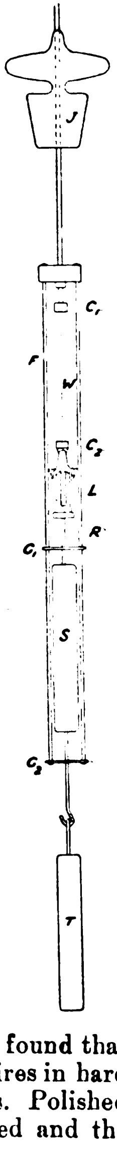
One or two modifications of the old testing apparatus were required to facilitate the removal of the test wire from the vacuum apparatus at different stages of deformation for the purpose of measuring the degree of deformation of the individual crystals. The modified form is shown diagrammatically in fig. 1. The ground glass joint J supports a wire frame F carrying two guides G which limit the movement of the tungsten and steel buoy T S. The test wire is attached to a clamp C_1 fixed to the ground joint J and to a clamp C_2, which may be linked to the top of the buoy by means of two sets of hooks as shown ; it may be connected or disconnected at will by floating the buoy and turning the ground joint J while in position in the vacuum apparatus. A loose sleeve L attached to the clamp C_2 serves to keep the test wire in line with the connecting rod R_1 of the buoy. The clamp C_1 is insulated from the metal frame F, and is electrically connected to a wire passing through the ground joint J ; the other electrical connexion is made through the mercury used in floating the buoy.

---

[*] A. E. van Arkel, Physica, v. p. 208 (1925).

[†] Bottger Z. Electrochemie, xxiii. p. 121 (1917).

Fig. 1.



The degree of deformation of the individual crystals in the test wires was measured in terms of the local reduction in diameter of the crystal. This was done by optical projection, the test wire being magnified about 40 times. The whole testing device was removed from the glass vacuum apparatus with the buoy disconnected. It was then mounted vertically in the projection apparatus in such a manner that the test wire could be rotated about its axis, and moved vertically with respect to the optical system. The deformed crystals could be photographed or measurements could be made directly by focussing on a ground glass screen.

Measurements of the extension of the test wire as a whole could be made directly through the glass of the vacuum apparatus by means of a cathetometer.

The methods of preparing sections of these crystals for purposes of X-ray and microscopic examination were the same as those described previously, with the exception that copper plating was substituted for the hard glass mounting in cases where it was necessary to retain the hardening effect of the deformation ; since it was found that the temperature required for mounting the test wires in hard glass was sufficient to remove some of the hardness. Polished sections of the deformed crystals were prepared and the copper dissolved off. These were then etched according to the same standard formula in all cases, viz., 1 minute in boiling hydrogen peroxide and 45 seconds in alkaline potassium ferricyanide.

The X-ray study was made with the same spectrometer and tube as those used previously, viz., a spectrometer of the photographic type and an X-ray tube emitting CuKα radiation. The X-ray beam was limited by a single slit parallel to the spectrometer axis, and by the area of the reflecting surface of the crystal. An undistorted crystal with a reflecting plane on the spectrometer axis will give a reflected image of that portion of the focal spot—usually about 1 mm. in diameter—from which X-rays may pass to it through the slit. Distortion of the crystals giving rise to changes in inclination of the reflecting planes will affect the length of the reflected spot, whereas alterations of the lattice parameter will only effect a shift of the reflected spot corresponding to a change in reflecting angle for any given wavelength. A small camera, 3 cm. radius, was used for the study of crystal distortion, whilst a camera of 6 cm. radius as well as one capable of adjustment to larger radii was employed for the study of variations in the lattice parameter.

The microscopic examination was carried out hand-in-hand with the X-ray measurements. Each section was photographed at a low magnification (× 150) as a check on the degree of deformation, and also at a high magnification (× 1000) for the purpose of structural examination. The photographs at high magnification were taken with a 3 mm. oil immersion lens (N.A. 1·3) under vertical illumination.

It was found necessary to anneal the individual crystals after they had been cut. For this purpose a special vacuum furnace was constructed. It was made up from flat tungsten strip formed into a long narrow tube closed at one end, into which the specimen was inserted. The temperature was measured by means of an optical pyrometer.

(3) *Crystal Hardening.*

The measurement of variations in the rate of deformation under given stress conditions offered the simplest if not the only means of investigating the hardening produced by the deformation of these small crystals. It follows from the theory of the formation of symmetrical wedge-shaped fractures established previously and illustrated by crystal models [*], that the area of the slipping planes at any stage of the deformation up to about 50 per cent. reduction of diameter will be approximately proportional to the local reduction of diameter perpendicular to the axis of the specimen and the line of intersection of the two sets of slip planes. Consequently in the case of a crystal deformed under constant load, the stresses on the slip planes will increase proportionally to this local reduction of diameter. Measurements on the rate of deformation under these conditions should therefore yield information concerning any variation of slip resistance which may occur during the different stages of deformation.

---

[*] Phil. Mag. xlviii. p. 800 (Nov. 1924).

Crystals whose deformation process closely approximates to the theoretical are easily realized in practice, the main differences being due to crystal distortion and to slight alterations in the mean crystal orientation during the deformation process when the crystals were unsymmetrically inclined to the wire axis before deformation. The combined microscopic and X-ray study of such crystals described in the previous experiments showed that, although bendings of the crystal planes may amount to changes of inclination of more than 20°, the mean lattice orientation was within 10° of being symmetrical to the wire axis in all cases. Further, it appeared that crystals deforming symmetrically from the beginning would not alter appreciably in their mean orientation throughout the deformation process. Photographs fig. 2 (Plate II.) and fig. 3 (Plate III.) illustrate the slightly unsymmetrical and the symmetrical type of deformation respectively. It is clear that the distortion will tend to alter the relation between the maximum local reduction in diameter and the area of the slipping planes in the sense that the areas of these planes will tend to be larger than those calculated.

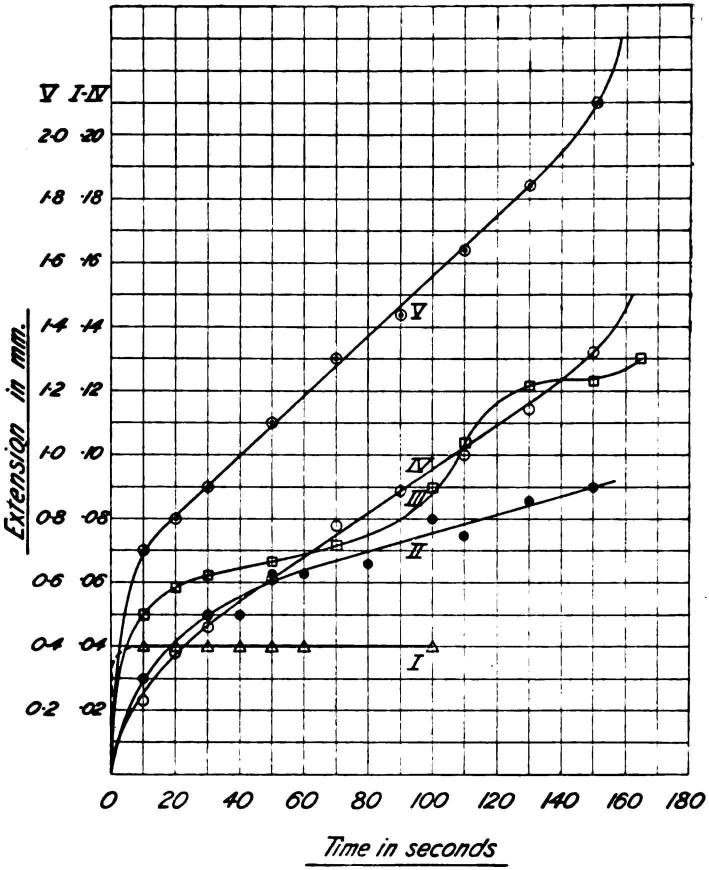
Measurements were made on the rate of decrease in the minimum crystal diameter for individual crystals in a large number of test wires when deformed under constant load at both 2000° K. and 1000° K. The loads in all cases were adjusted so as to produce fracture in times varying from one to ten minutes, the approximate values being calculated from the tensile strength temperature curves previously established*. The load was applied for equal increments of time at the given temperature and the local reduction of diameter measured after each application of the load. The results were plotted as local extension against time, the extension being calculated as 1·41 times the local reduction in diameter. The extension of the test wire as a whole was also measured in each case and plotted against the same time scale.

---

* Phil. Mag. xlviii. p. 229 (Aug. 1924).

Typical curves for the 2000° deformation under a load of 80 gms. are shown in fig. 4. Curve I shows the rate of extension of a crystal so inclined * that the stresses on one set of slip planes approached the maximum. In spite of this the deformation, which was rapid in the beginning, was reduced to zero. Curve II shows the rate of extension for a more symmetrically inclined crystal in which slipping

Fig. 4.



---

* The orientation of these crystals was judged by the shape assumed during deformation in accordance with the results recorded in fig. 36, p. 813, Phil. Mag. Nov. 1924.

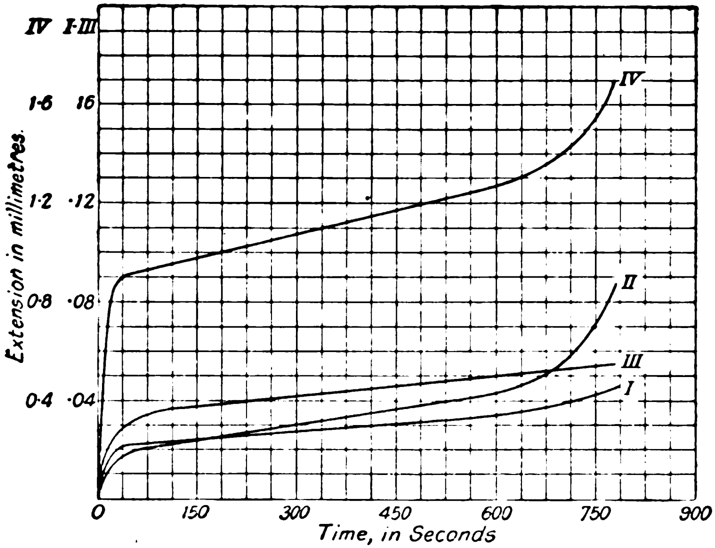
occurred on both sets of planes but more on one than on the other—the type shown in fig. 2 (Plate II.). In this case the deformation is not so rapid in the early stages, but is more rapid in the later stages than in I.

Curve III is an interesting and rather special case of a crystal which in the beginning was much like I, but in which owing to some favouring circumstances—possibly change of orientation—a second rapid increase in rate occurred followed again by a decrease in rate.

Curve IV is the normal time extension curve for a crystal deforming symmetrically from the beginning. It shows the smallest rate of flow in the early stages and the greatest in the later stages of deformation, and is the type which usually fractures; in fact. this particular crystal actually did fracture, as indicated by the rise in the curve after the last plotted point.

Curve V shows the rate of extension of the test wire as a whole. It is obviously the sum of the deformations of the individual crystals of the more symmetrical type, although some crystals of the unsymmetrical type must contribute to the initial deformations.

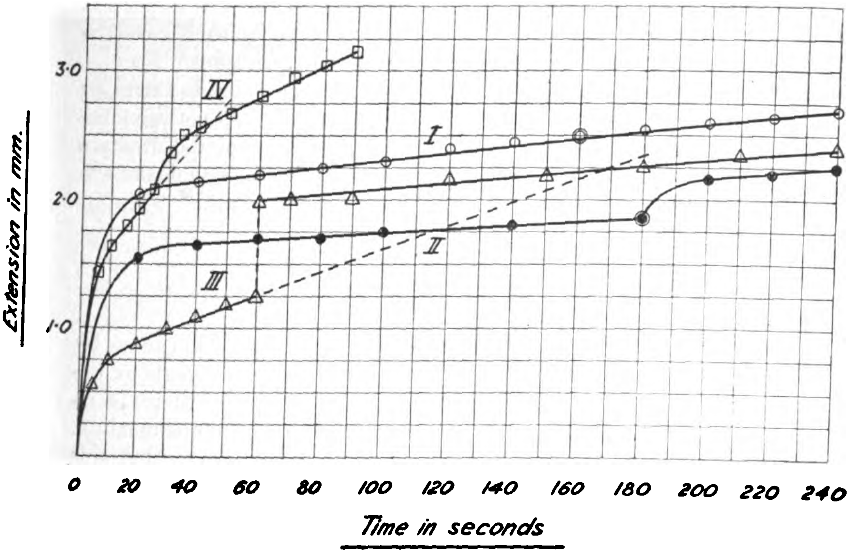
Fig. 4*a*.



Curves fig. 4 *a* show a similar set of observations for crystals deformed at 1000° under a load of 300 gms. Curves I–III show the rate of extension of three symmetrically deforming crystals, and curve IV that of the test wire as a whole. These curves show a change of rate which is greater than that taking place in similar crystals deformed at 2000°.

The most striking features of these curves are the rapid decrease of rate in the early stages of deformation and the marked tendency for the rate to attain a constant value in the later stages. The fact that there is a reduction of the rate in spite of increased stresses proves an increase in slip resistance or internal hardening of the crystal. The fact that deformation proceeds at a constant rate over a range of deformations in which the stresses on the slip planes must also increase at a constant rate, shows that the slip resistance under these conditions is also increasing at a constant rate.

Fig. 5.



The fact that the rate of extension of the test wire as a whole reflects the rate of the individual crystal, was utilized in studying further the effect of various factors on the degree of hardening; for instance, the effect of annealing and the effect of rate of deformation.

Curves fig. 5 show some typical examples of such measurements. Curve I shows the rate of extension curve of the test wire under constant load when deformed at 1000°. After the initial rapid deformation the rate of flow becomes absolutely constant. At an extension of 2·5 mm. the wire was heated to 1000° for a period of two minutes under no load and the original load again applied. The fact that the rate is unaltered shows that this heating has produced no measurable effect on the hardness. On the other hand, heating a similar wire to 1500° for the same time does remove some of the hardness, as shown in curve II. Curve III shows the effect of a rapid extension under an increased load for a very short time, the temperature of deformation being 2000°. The rate of flow under the original load is considerably reduced, which shows that the rapid deformation under increased stress produces a permanent hardening which must extend to unslipped portions of the crystal. The same effect may be produced by annealing at the temperature of the test—viz. 2000°—under no load and then applying the original load; the hardening is in this case increased without materially increasing the stress. This points to the rate of deformation as an important factor in the hardening process, although in each case the deformation is accompanied by increasing stresses.

The results of these measurements suggest that the straight line characteristic is due to some equilibrium between the three factors stress, temperature, and rate of deformation in their effect on crystal hardening. Similar conclusions to these have been reached by Polanyi and Schmid * working with tin single crystals.

(4) *Removal of Hardness.*

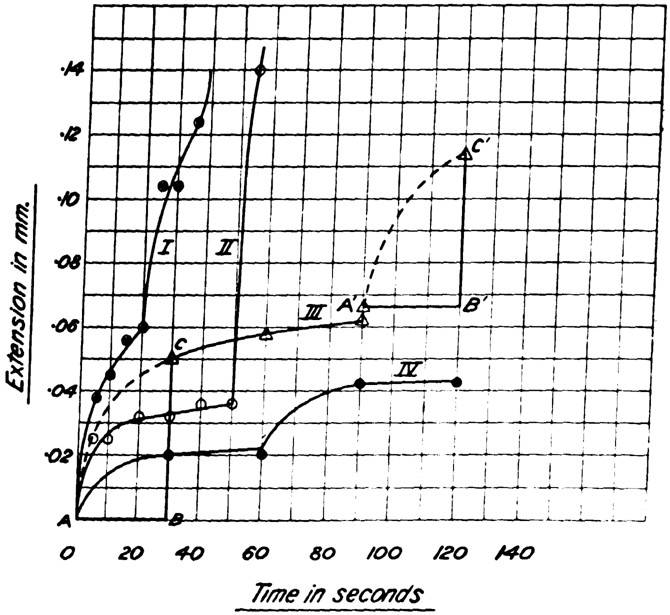
A quantitative estimate of the removal of hardness by annealing may only be obtained from measurements on the rates of flow of these crystals, provided that there is no change in mean crystal orientation during the annealing. Experiments to be described later clearly prove that this in fact is the case. The complete removal of hardness implies that equal stresses on the slip planes would produce equal flow velocities. We may therefore measure the rate of flow of a crystal under given initial stress conditions, allow the crystal to harden up as evidenced by a new reduced rate of flow, then anneal and reduce the stress in proportion to the degree of deformation and again measure the rate of flow; a comparison of the new rate with the original should give a measure of the hardness removal.

Preliminary measurements showed that a temperature of 2500° K. for 2 minutes was sufficient to remove the major portion of the hardness. Typical measurements are shown in the curves I–IV, fig. 6. Curve I shows the effect of annealing a crystal deformed at 2000°. After an extension of 0·06 mm. the curve repeats itself on adjusting the stress. Curve II shows the effect of leaving on the original load after annealing; a very much greater rate of flow than the original rate is produced by the increased stress, although this is only increased by 10 per cent. Curves III and IV

---

* M. Polanyi and E. Schmid, *Zeit. für Physik*, xxxii. p. 684 (1925).

Fig. 6.



were obtained with crystals deformed at 1000°. After annealing the mean flow velocity $\frac{C'B'}{A'B'}$, Curve III, is nearly equal to the initial velocity $\frac{CB}{AB}$, the ratio of the two being 0·95. Curve IV shows how the curves may be made to repeat themselves under readjusted stress after annealing. The results of a number of measurements on crystals deformed at 1000° and annealed at 2500° for 2 minutes are given in Table I. They show that the initial mean velocity of flow after annealing is on the whole less

TABLE I.

Before Annealing.				After Annealing.		Ratio of mean initial velocity before annealing to that after annealing.	
Applied Stress. Kg/mm².	Initial mean velocity. mm/sec. × 10^{-3}.	Constant Rate × 10^{-3}.	Local Reduction. Area per cent.	Applied Stress. Kg/mm².	Initial mean velocity. mm./sec. × 10^{-3}.		
10·0	0·7	0·03	8 .	10·0	0·7	1·00	Average ·86
10·0	2·7	0·35	22	10·0	2·3	·85	
10·8	1·67	0·18	23	10·9	1·63	·98	
10·7	0·9	0·03	15	10·6	0·63	·70	
10·8	1·4	0 03	19	10·8	1·30	·92	
10·0	1·53	0·03	21	10·1	1·13	·75	

than that before annealing by about 15 per cent. This probably does not mean that this degree of hardness is retained, as it has already been pointed out that there will be a tendency to adjust the new stress to too small a value owing to the crystal distortion. We may therefore consider that the hardness has been practically all removed by this annealing.

(5) *Crystal Distortion.*

The crystallographic nature of the distortion produced by the deformation of these crystals as well as the X-ray method employed in its measurement have already been described*. This distortion could only be explained as resulting from a break up of the crystal into fragments arranging themselves on curved surfaces which gave rise to an elongated reflected spot when a section of the deformed crystal was placed in a definite relation to the X-ray beam. For example, a section perpendicular to the wire axis through a wedge-shaped crystal fracture showed an elongated reflected spot when the minor axis of the section was mounted at the axis of the X-ray spectrometer, but no elongation was produced when the same section was mounted with its major axis in the same position. It appeared desirable to test the extent of this distortion at different stages of deformation of the symmetrically deformed crystals which have been investigated from the point of view of hardening and to study the effect of annealing.

Crystals in various stages of deformation were selected from test wires deformed under constant load at both 2000° and 1000° K. Sections were cut perpendicular to the wire axis in the region of greatest deformation, the wires in this case being mounted in hard glass. These sections were polished, etched, and examined for maximum distortion.

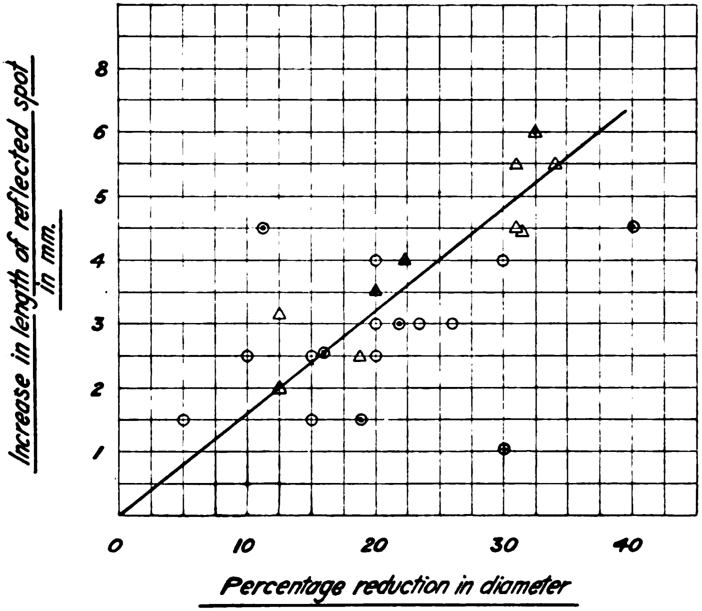
Photographs figs. 7 and 8 (Plates II. & III.) show typical sections of crystals deformed at 2000° and 1000° respectively. Below these, figs. 9 and 10 are photographs of the X-ray reflexions (× 2) obtained from the corresponding sections. They show a length of arc—due to a spreading of the X-ray beam—which is several times the length of the normal spot. It is to be noted that the arc is discontinuous in the case of fig. 9, whereas it is continuous in fig. 10.

The results of a number of measurements in terms of the increased length of the reflected spot in mm. are shown plotted against the percentage reduction in diameter in fig. 11. Although the observations are somewhat scattered there is clearly a correlation between the distortion and the degree of deformation, the distortion increasing in direct proportion to the degree of deformation. Further, the extent of the distortion appears to be the same for both types of crystal. In no case was the elongation of the spot zero, which proves that the distortion is distributed throughout the volume of the crystal in the region where slip is occurring.

---

* Phil. Mag. xlviii. p. 800 (Nov. 1924).

Fig. 11.



The extent of the distortion may be estimated in terms of the radius of a continuous curvature sufficient to cause the measured increase in length of arc. Calculations taking into account the dimensions of the specimen and the constants of the spectrometer show that a 6 mm. increase in length would be caused by a continuous curvature of about 0·7 mm. radius; this would represent a minimum curvature consistent with the actual reflexion.

The effect of annealing was tested by heating the test wire to 2500° for 2 minutes under no load after the required deformation. Examination of a large number of such annealed symmetrical crystals showed distortions in every way comparable with those produced in the unannealed crystals, the mean orientations being still symmetrical to the wire axis.

A few of the observations are plotted in fig. 11, the dotted circles representing annealed crystals which had been deformed at 1000° and the dotted triangles those deformed at 2000° K. A typical section of the latter type is shown in fig. 12 (Plate II.). Below, in fig. 13, is the corresponding X-ray reflexion; the arc is again discontinuous and of quite the same character as that of the unannealed specimen shown in fig. 9.

Owing to the divergence in the measurements of distortion as between one specimen and another, it appeared desirable to compare the distortion in the same specimen before and after annealing. For this purpose the special annealing furnace described in Section 2 was devised. No alteration of the spread could be detected as the result of annealing a number of such specimens at 2500° for a period of two minutes. Repolishing and etching so as to remove the old surface failed to produce any marked change other than that which would be expected on repolishing an unannealed specimen. Figs. 8 and 9 (Plates II. & III.) are photographs of the same crystal before and after annealing. The unannealed specimen was in this case copper-plated in order to avoid any heating during the preparation of the section, and the section was repolished and etched after annealing. Figs. 10 and 15 (Plate III.) show the corresponding X-ray reflexions. It is clear that this distortion is retained after annealing.

It is of interest at this juncture to record the effect on crystal distortion of a process of repeated extension and annealing, the stress being reduced after each annealing as in the case of the curves, fig. 6. The distortion of a crystal deformed in this way is plotted in fig. 11 as a crossed circle; it is clearly much less than a crystal extended the same amount under greater stresses. This would tend to show that the distortion is much more to be connected with the concentration of stress than with the mere process of deformation.

The fact that these crystals may be annealed at a high temperature without alteration of either orientation or distortion is in line with the results of experiments by Koref *, who has shown that fine tungsten single crystal wires may

---

* F. Koref, *Zeit. für Metallkunde*, Bd. xvii. p. 213 (1925).

be hardened by drawing and then annealed without any visible recrystallization.

(6) *Resolution of* CuKα *Doublet.*

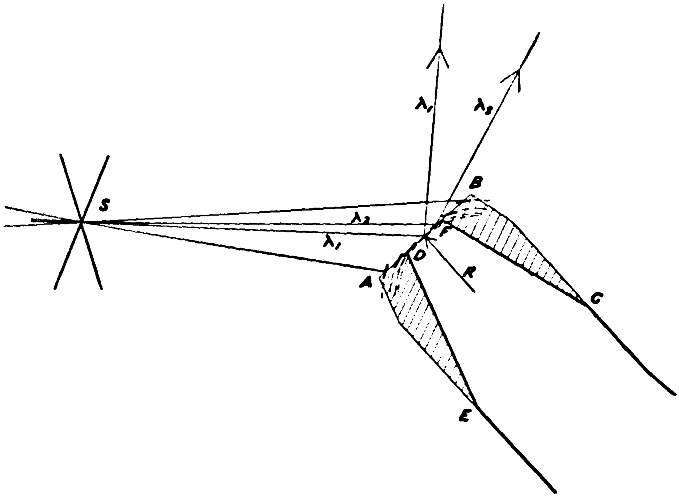
The extent of the distortion produced in these crystals suggests the desirability of measurements on the comparative resolving power before and after annealing. The resolving power may be diminished either by fineness of crystal size as shown by Debye and Scherrer, or by a lattice strain giving rise to a variable atomic spacing. The high degree of curvature into which these crystals have been deformed indicates a break up of the crystal into fragments which may be exceedingly small. The limiting size under these conditions will be determined by the degree of strain which the crystal lattice will stand without breaking up. It is fair to assume that this strain will not be greater than that corresponding to the elastic limit of the material, and it may be much less. This strain in the case of the pure tungsten crystal deformed at 1000° is only 0·025 per cent., the calculation being based on special measurements of Young's modulus and the elastic limit at this temperature. On the other hand, the lattice strain corresponding to the elastic limit of a Pintsch single crystal wire will be 0·18 per cent. according to van Arkel. The former is probably below the limits of accuracy of present day X-ray methods but the latter is not, as van Arkel has demonstrated by the use of very fine wires. It seemed worth while to compare the resolving power of these pure tungsten single crystals with that of Pintsch single crystals deformed (in a similar manner) at room temperature as a check on the elastic strain hypothesis. Should the pure tungsten crystals show a diminished resolving power which is comparable with that of Pintsch crystals, it would be fair to assume that its cause was crystal break-up rather than lattice strain, in which case an increase in resolving power on annealing must be associated with a coalescence of these small crystal fragments.

The symmetry and degree of distortion produced in wedge-shaped fractures suggest a suitable arrangement for obtaining good resolution of a monochromatic X-ray beam. It has already been pointed out that the distortions in such wedges are crystallographic in nature. They are such that the (110) planes of adjacent fragments tend to lie on approximately coaxial surfaces the axis of which is perpendicular to the wire axis and parallel to the wedge

edge, the surfaces being convex towards the wedge edge. This is shown diagramatically in fig. 16.

A B represents a section of the wedge cut at right angles to the wire axis. The dotted lines represent the concentric surfaces which intersect the plane of A B at angles which vary as shown. It is clear that an X-ray beam composed of one wave-length λ_1, and divergent from a slit S, will only reflect from a narrow portion of the section at D when A B is fixed at the appropriate angle for the reflexion of λ_1. A second wave-length λ_2 will be reflected from a second portion of the section F which makes the appropriate angle of reflexion for the corresponding part of the X-ray beam.

Fig. 16.



Suitable conditions for the comparison of the resolving powers of both the pure tungsten and the Pintsch single crystals were realized in practice. Crystal wedges (Pl. V fig. 17) were obtained on fracturing Pintsch wires at room temperatures. These were quite comparable with those obtained by fracturing the pure tungsten wires at 1000° (fig. 18). Annealing the specimens produced no marked effect on the crystal distortions, which in all cases were symmetrical with the wire axis, and which amounted to a gradual change in inclination of the (110) planes through at least 20° in the case of the pure tungsten crystals and 10° in the case of the Pintsch crystals. Typical sections through these wedges are shown in figs. 19–22. Fig. 19 is from an unannealed specimen of pure tungsten prepared by mounting in copper. Fig. 20 is from a similar specimen which had been annealed at 2500° for two minutes, then mounted in hard glass. Figs. 21 and 22 (Plate V.) are from the same Pintsch wire before and after annealing respectively. Below these in figs. 23–26 (Plates IV. & V.) are photographs of the spread in the X-ray beam obtained from the corresponding sections.

The resolving powers of two crystals such as those in figs. 19 and 20 (Plate IV.) were compared by mounting the sections side by side with their major axes on the axis of the spectrometer using Cu Kα radiation. Exactly similar reflexions giving a well resolved doublet were obtained in all such cases. Fig. 27 is a photograph of typical reflexions enlarged five times.

The accuracy of lining up of the two crystals does not permit comparison of the absolute magnitude of the atomic spacing, but it may be claimed that there is no measurable difference in line breadth in the two cases. Comparing the resolving power of Pintsch single crystals before and after annealing always showed a non-resolved reflexion before annealing and a well resolved reflexion after annealing. The two photographs in fig. 28 (Plate V.) are typical of such reflexions. The increase in line breadth necessary to cause the non-resolution must correspond to a change of reflecting angle of at least 0·05 per cent. and probably more.

In order to be sure that the fuzziness was not produced by some alteration in crystal distortion too small to effect the spread and which would reduce the reflecting surface on annealing, a number of crystals in the hard state were ground in such a way as to limit the reflecting surface to a long narrow zone about 0·02 mm. in width*, the crystal being ground to a chisel-edge as shown by the unshaded portion in fig. 16.

Mounting these edges on the spectrometer axis and rocking produced non-resolution in all cases until after the crystals were annealed, they then resolved as they should.

In order to test for any possible shift in the mean atomic spacing due to the deformation process, a precision measurement of the mean reflecting angle for the reflexion of the Cu Kβ line was made before and after annealing. No measurable change was observed within the limits of experimental error, which was probably under 0·05 per cent.

---

* The spectrometer arrangements were such that a surface ·02 mm. in width rocked at the axis was sufficiently small to give good resolution. This was actually tested by mounting a recrystallized wire of this dimension on the spectrometer axis and rotating through several degrees; good resolution was easily obtained.

(7) *Microscopic Examination.*

The chief results of the microscopic examination, which was carried out hand in hand with the study of distortion by the X-ray method, will now be considered.

The crystals deformed at 2000° gave discontinuous X-ray reflexions which showed that the crystal had been broken up into relatively large fragments or groups of fragments even before annealing. Microscopic examination confirmed this conclusion and gave additional information in regard to the nature of the break up. It showed that the break up was crystallographic in nature in the sense that boundaries tended to lie along definite crystal planes. The boundaries appeared in all cases as lines parallel to the major axis of sections cut perpendicular to the wire axis, and therefore correspond to lines of intersection of two sets of (112) slip planes. It was more difficult to detect their direction in planes cut perpendicular to these sections along lines parallel to their minor axes, although in extreme cases it could be seen that they did not follow the slip plane as might be expected, but rather appeared as irregular splits more nearly inclined at 45° to the wire axis. Photographs figs. 29–30 (Plate IV.) illustrate this point. Fig. 29 is from the same annealed crystal as that shown in fig. 12, which clearly shows the vertical lines of break up in the planes perpendicular to the wire axis. Fig. 30 is from a similar unannealed crystal cut in a plane perpendicular to this section and to the vertical boundary markings. The line connecting the projecting portion of the crystal in the upper left-hand corner with the niche in the lower right-hand corner of the photograph is the trace of the (112) plane on which a large slip or series of slips has occurred—such as can be seen in fig. 2. There is no indication of a boundary marking extending in this direction, but the long marks inclined at about 45° and ending in this niche doubtless are the boundary markings in this case. Results such as these rather point to the conclusion that the deformation process is accompanied by a type of recrystallization at this temperature.

Crystal wedges produced by the fracture of single crystals at this temperature show this break up in a very marked degree. In sections of such crystals cut perpendicular to the wire axis as many as 10 vertical markings have been counted and the X-ray reflexion has shown as many as 15 discontinuities in some cases. The number and character of these is unaffected by annealing.

No such obvious evidence of break up occurs in the case of crystals deformed at 1000°, although in the extreme case near the tip of crystal-wedge fractures one or two markings are to be found which are similar to those found in the 2000° wedges. These crystals, however, show very marked differences in etching effects before and after annealing. Although the character of the etch markings remains unchanged, a marked differential rate of etching—evidenced by differences in level—occurs in the case of the unannealed crystal which does not occur on repolishing and etching after annealing. The effect is also most marked in the case of the crystal wedges. Photographs 31–34 (Plates III. & IV.) illustrate this. Figs. 31 and 32 are of the sections shown in fig. 8 and fig. 14 (Plate III.) respectively. Figs. 32 and 34 are sections of the same crystal wedge before and after annealing respectively—the crystal having been repolished and etched after annealing. It is to be noted in this case, that although the differences of level occurring in fig. 33 do not occur in fig. 34, the change in orientation of the lamellæ is just as marked in the annealed specimen as in the unannealed, which confirms the results of the X-ray measurements of distortion.

The Pintsch single crystals showed no marked difference before and after annealing, which is probably due to a masking of the effect by the thorium oxide present in these wires. Figures 35 and 36 (Plate V.) are from the same crystal before and after annealing. The larger number of black dots in figure 36 has probably not been produced by the annealing, as a number of sections of unannealed crystals showed similar markings.

(8) *Discussion of Results.*

The chief interest in the results of these experiments lies in their bearing on the theories of hardening accompanying deformation and the possible existence of residual lattice strain in a worked metal.

The most important results appear to be the persistence of crystal distortion after annealing and the improvement in resolving power on annealing distorted Pintsch single crystals. The former implies a broken up state which is not altered sufficiently by annealing to re-establish a new perfect single crystal and that the break up is not, therefore, the cause of hardening. If we accept this view, it suggests that the cause of the production of fuzziness is the cause of hardening even though it may only be measured in extreme cases.

The cause of fuzziness—as in van Arkel's experiments—is limited either to the size of fragment into which the crystal is broken up or to a disorganization of the crystal lattice within the broken up fragments. The size of crystal required for a broadening of line equivalent to a variation in reflecting angle of 0·1 per cent. would be of the order 10^{-5} cm. as calculated from the theory of Debye. Although it would be difficult to prove that the broken up fragments are not as small as this in the case of the Pintsch wire, the experiments on the pure tungsten crystals indicate that there is a tendency toward lattice preservation which would render it improbable. The 2000° deformations produce a break up which can be seen under the microscope and the 1000° deformations do not produce a break up sufficient to give non-resolution of the Cu Kα doublet, although the crystal distortion appears to be sufficient to do this were no other cause operative in maintaining lattice continuity*. On the other hand, we have the agreement between the degree of fuzziness and the strain corresponding to the elastic limit for two cases of the same material. The results, therefore, point to elastic strain rather than crystal size as the cause of fuzziness.

Viewed in the light of elastic strain as the cause of increased slip resistance, the rapid increase of hardness in the early stages of deformation would be accounted for by the early setting in of a distortion which involves a bending of the crystal fragments as well as the production of lattice discontinuities. These bendings would involve equal amounts of extension and compression, which is in agreement with the X-ray measurements. The building up of the progressively increasing curvatures without progressive increase in hardness could be accounted for without assuming that the strain in these fragments increases in proportion to the degree of deformation, as the degree of break up can be brought in to account for this. It is to be expected that the degree of strain would increase with increase of stress, which is in accord with the fact that hardness increases with increase of stress under conditions of constant rate of deformation. The effect of time and temperature on the degree of hardness would appear to be associated with the tendency of the lattice to maintain itself in the unstrained state, the extent of the restitution depending on the temperature and the degree of strain. The differences in rate of etching before and after annealing would on this view be associated with differences of residual elastic strain.

---

* The radius of curvature of the distorted crystal may be as small as 0·02 mm. Crystal lamellæ bent to this radius cannot be thicker than 2×10^{-5} cm. if they show no change of atomic spacing exceeding 0·025 per cent.: viz., the measured value. This is of the order of magnitude required by the theory of Debye for non-resolution of the Cu Kα doublet.

XXIII. *Improved Grating for Vacuum Spectrographs.*
By R. W. Wood *and* Theodore Lyman *.

[Plate VI.]

ONE of the difficulties attending the use of concave gratings in vacuum spectrographs is the oxidation or corrosion of the polished metal surface by active vapours from the discharge-tube. This can be in part prevented by constructing the spectrograph in such a way that the vapours are pumped out through a port immediately behind the slit (T. Lyman, 'Astrophysical Journal,' lx. p. 1, 1924).

The suggestion was made by one of us in a note published in this Journal in September 1924 that glass gratings would be found more suitable than metal, as they could be cleaned without difficulty. One such grating of one half metre radius had been successfully ruled and etched at the time, but it was destroyed by fire before any tests were made with it. The original plan was to coat the glass grating with a film of metal by cathode discharge. This film could be easily renewed from time to time, if necessary. On discussing the matter, however, shortly after the publication of the paper above referred to, we came to the conclusion that it would very probably turn out that the surface of the glass would have a reflecting power superior to that of metals in the region of the shortest wave-lengths. This surmise we based on the fact that the decreasing reflexion coefficients of metals and the increasing coefficients of transparent substances (with decreasing λ) practically meet in the neighbourhood of wave-length 2000.

Pressure of orders for speculum gratings have kept the two dividing engines of Johns Hopkins University so busy that it was not until this spring that experiments with glass gratings were commenced again.

Three have been made already, two four-inch ones of one metre radius, and a five-inch one of two metres radius. They were ruled with a very light pressure of the diamond to avoid the wear which inevitably destroys the ruling-point if it is operated under sufficient pressure to secure brilliant spectra, and then etched by the method described by one of us (R. W. Wood, "Intensification of Glass Gratings, Phil. Mag., December 1906) twenty years ago.

---

* Communicated by the Authors.

The concave mirror showed practically no spectra at all when it came from the ruling engine. In bright sunlight it was just possible to see the ruled surface, which is probably traversed by extremely narrow deep cracks. Dilute hydro-fluoric widens these by eating away the edges, and produces a corrugated or undulating surface which gives bright spectra. Too much etching causes a diminution of the brilliancy. To obtain the proper amount of etching to give the maximum brilliancy the same method was employed as that described in the paper referred to above—namely, to dip one corner of the grating into the acid to the depth of about 3 mm. for five seconds, and then wash and dry it. On examination the etched corner is found to be much brighter than the rest of the surface. The whole grating surface is now immersed face down in the acid for five seconds, washed, dried, and again examined. It now shows the same brilliancy over its whole surface as that exhibited by the corner in the first instance, but the corner is usually found to be much brighter than the rest. A third bath of five seconds is given and the process repeated until the whole surface has been brought up to the brilliancy of the corner. This is the point at which to stop, as further etching produces no improvement and eventually weakens the intensity.

One of the glass gratings of a metre radius has been tested in a vacuum spectrograph at Harvard. The ruled surface measures 5×8 centimetres, there are 15,000 lines to the inch. Spectrograms obtained in the first order of a concave grating ruled at Johns Hopkins on speculum served as a means of comparison. This speculum grating was almost identical in dispersive power with the instrument under test, though its ruled surface was not quite so large, measuring 3·1×7·8 centimetres. It differed also from the glass grating in that it possessed a strong second-order spectrum. It had been in continuous use in the vacuum spectrograph for more than 18 months, but showed little decrease of reflecting power in the extreme ultra-violet—a fact interesting in itself.

The region examined extended from 1900 A.U. to the limit of the spectrum. For the upper part of this range a hydrogen discharge-tube was employed, while on the short wave-length side of 1300 A.U. a vacuum spark, either between copper or tungsten terminals, was used.

It is impossible to say anything very definite as to the relative efficiency of the two gratings between 1900 and 1300 A.U., for in this region it was necessary to compare two sets of spectrograms taken on plates of quite different photographic behaviour, and at dates separated by nearly a year. It appears probable, however, that on the long wave-length side of 1400 A.U. the speculum grating has the advantage.

On the other hand, a very positive statement may be made concerning the behaviour of the two instruments in the range between 1300 A.U. and the limit of the spectrum, for in this region all spectrograms were obtained under the same conditions and on dates separated by but a few days.

As a result of these experiments, there can be no doubt whatever that the glass grating produces a much more intense spectrum on the short wave-length side of 500 A.U. than that obtained from speculum. This superiority is particularly pronounced in the region of the very shortest wave-lengths between 300 and 200 A.U.

It appears, therefore, that glass gratings will prove very useful in vacuum spectroscopy, since their reflecting power for light of very short wave-lengths is higher than that of similar instruments ruled on speculum and is not likely to change with time.

Thus far only a grating of 15,000 lines to the inch has been tested in the vacuum spectrograph, but two of 30,000 lines have been ruled and etched, and appear to be satisfactory. Experience has shown that gratings ruled with the 30,000 spacing on speculum metal are very much less brilliant in the region of very short wave-lengths than the 15,000 gratings. This is probably due to the complete removal of the polished surface. In the case of the glass gratings it is expected that this trouble will not be found, as the etching process probably gives the same type of undulating surface in both cases.

The spectra in Plate VI. were taken with the high vacuum spark between copper terminals. The upper spectrum was made with the speculum grating, the lower was obtained with the grating on glass. The time of exposure was the same in both cases.

The relatively great intensity of the violet region in comparison with the red, in the case of the glass gratings, is very marked when the grating is held in sunlight, and the spectrum focussed on a white screen.

XXIV. *On the Origin of the E.M.F. of a Photoelectric Cell, containing a Fluorescent Electrolyte.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I WISH to make some remarks suggested by the very interesting work of Mr. W. Rule (Phil. Mag. (7) i. p. 532) on the variation of the E.M.F. of photoelectric cells containing a fluorescent electrolyte, when the amount of the fluorescent material is changed.

Mr. Rule admits that the electrometric measures furnish always the value of the E.M.F. of adsorption, and neglects thus the Becquerel effect which, as I have pointed out (*Comptes Rendus*, t. clxxvii. p. 395, 1923), is superposed on the latter, chiefly in the cells provided by very concentrated fluorescein.

Each E.M.F. measured is also the algebraic sum of two quantities varying in different ways with the illumination time; so are explained the inflexions presented by the curves of Mr. Rule, when the concentration is great.

In his experiments, the E.M.F. attains a constant value in 40 minutes, but in dilute solutions; however, it is possible to separate the effect produced in the mass of the liquid by screening the light; the maximum reached by the E.M.F. in darkness is independent of the initial electrical conditions of the experiment (*Comptes Rendus*, t. clxxx. p. 1102, 1925; *Soc. Française de Physique*, No. 217, p. 73 s, 1925).

For the same reason, I do not see any discrepancy between the absence of an E.M.F. in a cell containing a pure sodic solution only, and the existence of an E.M.F. produced by the light emitted by a very fluorescent solution itself, which illuminates the electrode protected against the direct light of the quartz lamp. It is a Becquerel E.M.F. whose sign is contrary to that of the new effect I have described, and which is the subject of Mr. Rule's research. A proof of this is that the positive E.M.F. in the contested experiment vanishes in the darkness and the negative effect subsists alone.

Moreover, I will remark that a cause of mistake in the measures of conductivity of fluorescent electrolytes is to be found not only in the Becquerel effect, if an electrode is illuminated, but also in the E.M.F. produced by the illumination of the liquid mass which arises if the apparatus is not disposed in a strictly symmetrical manner in the light pencil.

Yours faithfully,

A. GRUMBACH.
Professeur à l'Université de Nancy,
Institut de Physique.

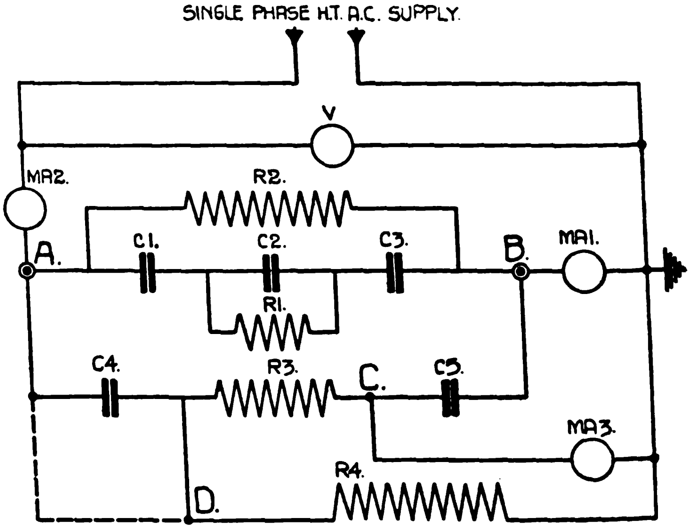
Nancy, France.
June 11, 1926.

XXV. *On the Determination of the Current Voltage Characteristic of a Siemens Ozonizer.* *By* R. WINSTANLEY LUNT, *M.Sc., Ph.D.,* 1851 *Exhibition Senior Student*[*].

WHEN using a Siemens ozonizer, that is to say an ozonizer formed from concentric cylinders of glass or other insulator, it is not infrequently desirable to cool either one or both electrodes in order to reduce thermal effects to a minimum.

This is most simply achieved by allowing a stream of tap-water to flow through a thin-walled glass vessel in contact with, or immersed in the mercury or other conducting material constituting the electrodes. When such a device is employed considerable care must be exercised in choosing the electrical connexions appropriate to the determination of the true current flowing through the ozonizer and the voltage associated with it.

A typical circuit in which an ozonizer is connected to a source of high-tension alternating current is represented, using the usual conventions, in the following diagram.



The ozonizer is represented by three capacities in series[†]: the capacity C_1 of the inner cylinder of dielectric, the capacity C_2 associated with the annular space containing the gas subjected to the discharge being in parallel with a resistance R_1 representing the inverse of the conductivity of the gas due to gaseous ionization, and the capacity C_3 of the outer cylinder of dielectric. A and B denote the electrodes.

---

[*] Communicated by Prof. F. G. Donnan, F.R.S.

[†] *Cf.* Phil. Mag. xlix. p. 1238 (1925).

The glass or other insulating surface separating the electrodes possesses a leakage resistance represented by R_2, which may easily be maintained of the order of 10^2–10^3 megohms, so that this leakage current is in general negligible.

The column of water connecting the tap, or water supply, to the high-tension electrode A through C_4 offers a leakage resistance denoted by R_4.

A glass vessel carrying cooling water in contact with the high-tension electrode A is associated with a capacity C_4 in series with a resistance R_3 which arises in the stream of cooling water flowing between the electrodes. Similarly, the glass vessel in contact with the low-tension electrode introduces a capacity C_5 between the cooling water and this electrode.

If the circuit be not earthed at the point C, then the system C_4, R_3, C_5 forms a current path in parallel with the ozonizer; the current read by the milliameter MA_1 is therefore greater than that carried by the ozonizer. It has been found that the error due to this current is not generally negligible.

A convenient method of earthing the circuit at the point C has been achieved by allowing the stream of cooling water to flow through a short length of copper tubing immediately before entering the cooling vessel immersed in, or in contact with, electrode B. To this copper tubing is soldered a lead connecting to earth. The potential across C_5 is thereby reduced very nearly to zero, and is due solely to that arising from the current through MA_1 and the resistance of that instrument. It is therefore of the order of one or two volts.

The voltage applied to the ozonizer is read on the high-tension voltmeter V.

In a number of experiments carried out in these laboratories, it has been observed that the total current in the high-tension line as indicated by the milliammeter MA_2 is equal to, within the limits of experimental error, the sum of the current flowing through the ozonizer as indicated by the milliammeter MA_1, that flowing through C_4R_3 indicated by the milliammeter MA_3, and that flowing through R_4, thereby indicating that no sensible current flows through C_5.

It may not be out of place to mention two methods that have been found to obviate a difficulty that arises in the cooling of the high-tension electrode. It is obvious from the diagram that unless the impedance of the capacity C_4 be much lower than the resistance R_3, the condenser C_4 will be subject to a strain due to the major portion of the impressed voltage. That is to say, the glass walls of the vessel carrying the cooling water to the electrode A have to withstand a voltage of the order of the applied voltage. In practice it has been found that frequently the dielectric strength of glass is inadequate to this stress. Satisfactory results can be achieved by constructing this vessel of fused silica.

An alternative method that is practicable when a silica vessel is not available consists in connecting the electrode A to the stream of cooling water, in the manner adopted at the electrode B, at the point of entry to, or exit from, the cooling vessel associated with the electrode A, represented on the diagram by D, a dotted line indicating this connexion. It is then necessary to arrange for a long and well insulated column of water to connect the cooling vessels in order that the current carried by this column may be conveniently small.

When it is necessary to determine the heat transferred from the high tension electrode to the cooling water, further precautions must be adopted. These consist in providing two short lengths of copper tubing, each connected to the electrode A, in the stream of cooling water. One is placed at the point where the stream enters the cooling vessel and the other at the exit therefrom. No appreciable current can then flow through the water in the cooling vessel. It is important to note that the thermometers which indicate the temperature of the stream must be introduced into the stream between each copper tube and the cooling vessel.

The William Ramsay Laboratories of
Physical and Inorganic Chemistry,
University College, London.

XXVI. *A simple Vacuum Arc Mercury Still for Laboratories. By* H. P. Waran, *M.A., Ph.D., D.Sc., F.Inst.P., Additional Professor of Physics, The Presidency College, Madras* *.

MERCURY, so largely used in laboratories in connexion with so many experiments, gets contaminated very easily by contact with foreign materials rendering it unfit for further use until it is purified again. There are many ways of cleaning it, but none so satisfactory as distilling it *in vacuo.* The usual process so largely adopted of shaking it with dilute nitric acid or passing it as a fine spray through a column of dilute nitric acid, is not only very wasteful but the mercury requires further washing and drying before it is ready for use. Even then the product can never be regarded as so good as distilled mercury.

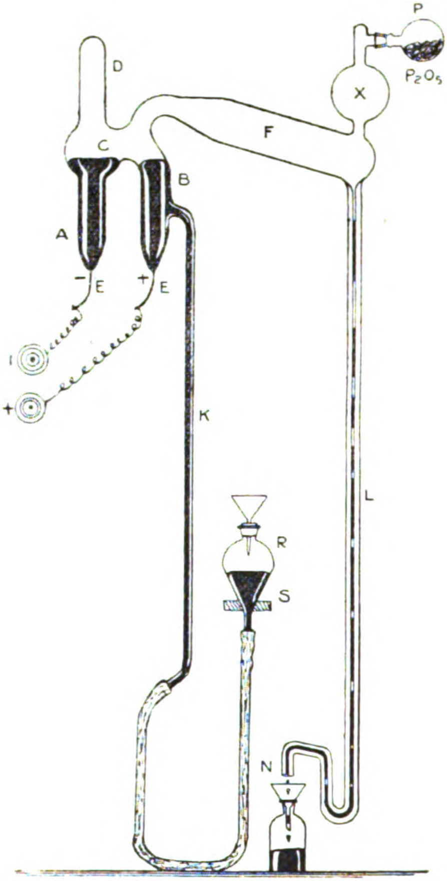
The distillation of mercury, like the distillation of any other liquid, can easily be done in retorts of iron or pyrex glass that can stand the temperature of 357° C., the boiling-point of mercury at atmospheric pressure. The distillation, if conducted *in vacuo,* yields a product distinctly purer, as the mercury will boil off at a very much lower temperature and thus be free from any volatile impurities that may come along with it at a higher temperature. To distil the mercury *in vacuo* there are many forms of apparatus on the market, but a very convenient form of it that has been found to be quite good is the one shown in fig. 1, and though the arc pattern of it is in no way new, still the present form has many other interesting and useful features as well to recommend it for general use in laboratories.

ACB is an inverted U-tube with sealed-in platinum electrodes E and E′. The limb A has a short vertical prolongation D, about ten centimetres long, which serves as an auxiliary condenser for the negative limb A. To the limb B is attached a large air-cooled condenser F formed out of a thin-walled tube about 1½ inches in bore and about 8 inches in length. From the other end of F two tubes branch off. The vertically downward branch L is a capillary tube of not more than 2 mm. bore and over 100 cm. in length, bent round at the lower end as shown at N. The upward branch has a bulb, and it terminates in a conical ground joint to which a bulb P containing P_2O_5 is attached with vacuum grease. From the side of B there is a vertically downward tube K

---

* Communicated by the Author.

Fig. 1.



about 70 cm. in length, and its lower end is connected to a mercury reservoir R by a 4 foot length of pressure tubing. The whole of the apparatus is mounted on a backboard of wood which is attached to a vertical wall in any convenient corner of the laboratory. The platinum electrodes are soldered to lengths of copper wire leading to terminals on the board which are connected to the mains through a 10 ampere fuse and switch. An adjustable resistance is also included in the circuit so that the current may be adjusted within the limits of 8 and 4 amperes. This mercury arc still operates as follows.

The switch being off, the mercury reservoir R is raised until the mercury rising in B overflows into F. This thin stream of mercury breaks into drops on reaching the upper end of L, and during their passage down L these drops of mercury trap air from the system, and by a Sprengel pump action the system is rapidly exhausted. The mercury overflowing at the delivery end N is caught and poured back into R at this stage. In a few minutes a vacuum of the order of less than a tenth of a millimetre of mercury is reached inside the apparatus, the phosphorus pentoxide in P being essential to remove the water vapour liberated as the mercury and the glass walls get heated up under the arc. The mercury reservoir is now restored back to its shelf S and the current is switched on immediately. By the lowering of the mercury level in B, as the contact with the mercury in A is broken at C, an arc plays between the two pools of mercury in A and B and the mercury is rapidly vaporized, the amount evaporated from the negative limb being much less than that evaporaled from the positive limb. A part of it condenses in D, and is returned to the limb A where the mercury remains for ever at a constant level. Much of the vapour, however, goes down into F, where by air-cooling it condenses and trickles down into L, where the Sprengel pump action continues to keep the condenser and arc space highly exhausted automatically, a condition necessary for the efficient working of the arc and the evaporation of the mercury at the lowest temperature. As the distilled mercury comes down L it displaces out the small quantity of dirty mercury that was in it. After returning the yield of mercury during the first ten minutes back into the reservoir, the mercury dropping out at N may be collected as dry distilled mercury of a very high degree of purity.

Once the arc distiller has been set up in this way and the vacuum sucked up by itself, all that one has to do is to pour in dirty mercury at R, raise the mercury reservoir a few centimetres to establish a momentary contact with A, and then restore it back to its shelf.

The breaking of the contact at C starts the arc, and the mercury distils over merrily and flows out at N in drops, the progressive fouling of the vacuum by the gases liberated by the dirty mercury being automatically pumped out by the Sprengel action at L.

One or two arc distillers of this type set up in physical laboratories have the great advantage that in addition to supplying pure mercury for accurate experimental purposes, the arc can also be used as a bright source of light for many optical experiments. In such cases, the distilled mercury is only a bye-product in the operation.

Arc distillers of this type are now being made and sold by Messrs. Baird & Tatlock (London) Ltd., 14–15 Cross Street, Hatton Garden, London, E.C. 1. Two distillers of this type in operation in my laboratory taking 5 amperes at 60 volts have been found to have an average yield of 1½ lb. of distilled mercury per hour, or approximately 2 grms. of mercury per watt hour.

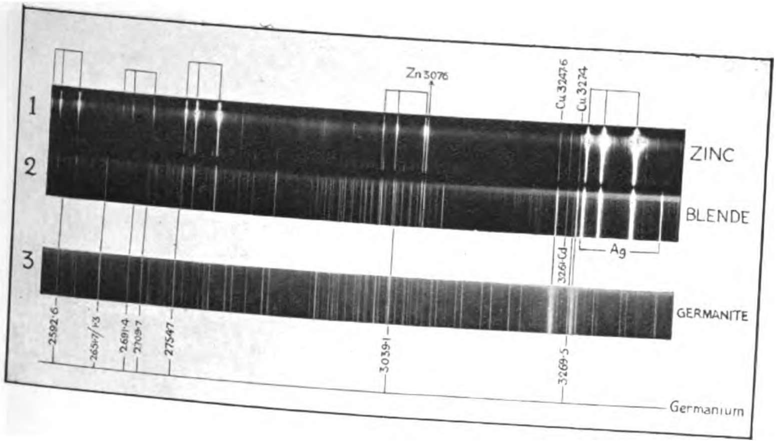
The yield can of course be increased by eliminating the auxiliary condenser D and fitting the negative limb also with a reservoir. In this case the platinum electrode seals E and E′ can be eliminated and the current introduced through the two reservoirs. Further, the condenser F can also be replaced by a water-jacketed one cooled by a circulation of water. The vapour pressure inside can thus be kept low even with a higher current through the arc with a corresponding increase in the output of distilled mercury per hour. But the arrangement is complicated and is not to be recommended for the average laboratory use.

NOTE.

The Publishers regret the omission of Plate XVI. A, illustrative of Mr. W. SCUTT's Paper "On Germanium in a British Mineral," in the May Number, vol. i. p. 1007.

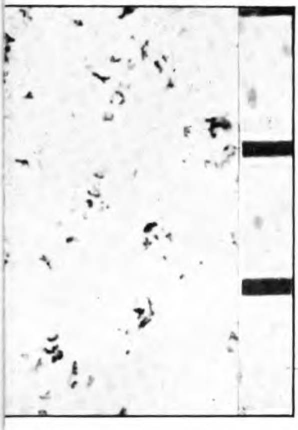
[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

This Plate should of course be bound with Vol. I. 1926.


Zn 3076
Cu 3247·6
Cu 3274
1
2
ZINC
BLENDE
Ag
3
3261·Cd
GERMANITE
2592·6
2651·7/1·3
2691·4
2709·7
2754·7
3039·1
3269·5
Germanium

·5 ; quartz ocular 20.

e, ap. 1·25 ;
ision of the



NY (not spherical).

romatic objective, n. a. 1·25 ;
: 1800. 1 division of the
x.)

8

9

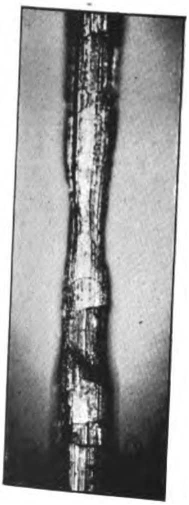


FIG. 2.

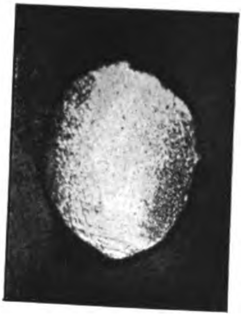


FIG. 7.

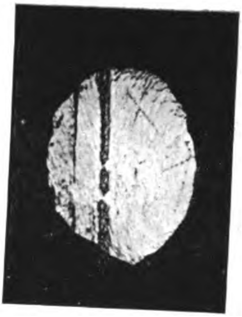


FIG. 12.

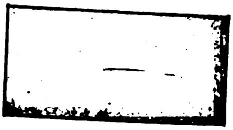


FIG. 9.

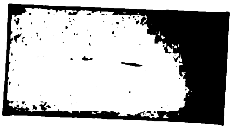


FIG. 13.

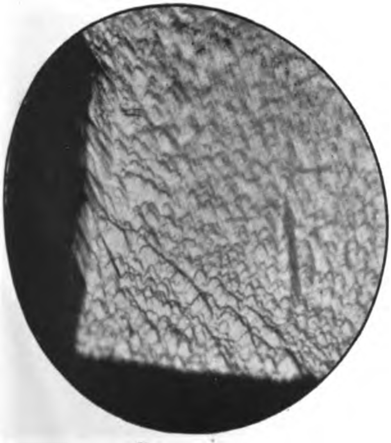


FIG. 30.

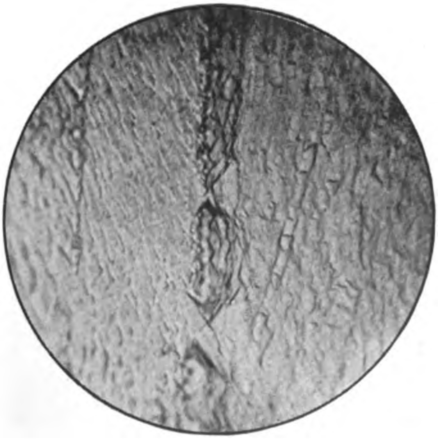


FIG. 29.

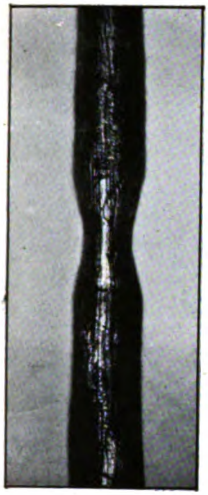


FIG. 3.

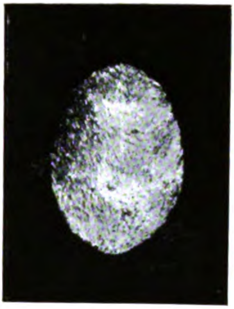


FIG. 8.

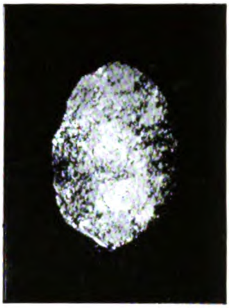


FIG. 14.

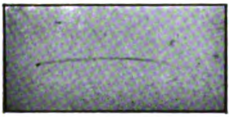


FIG. 10.

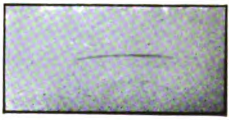


FIG. 15.

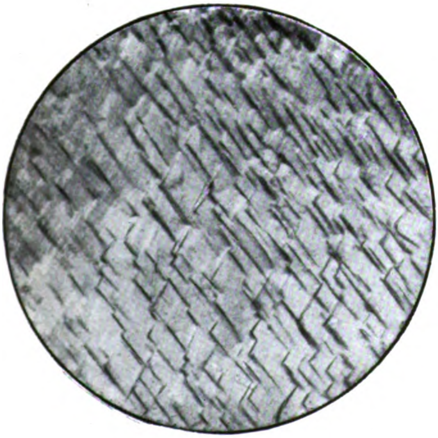


FIG. 31.

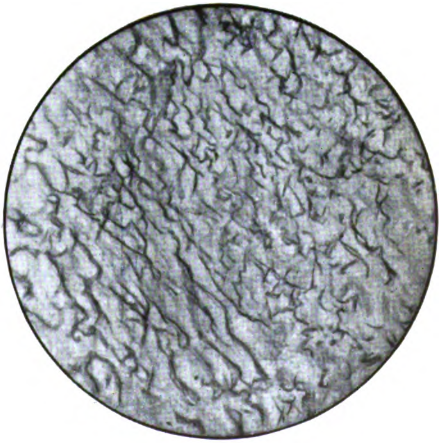


FIG. 32.

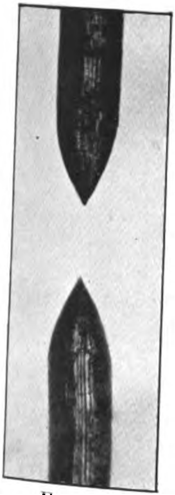


FIG. 18.

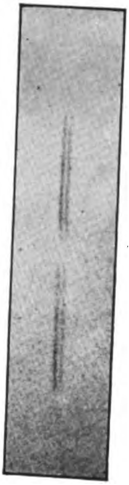


FIG. 27.

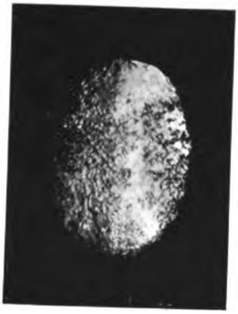


FIG. 19.

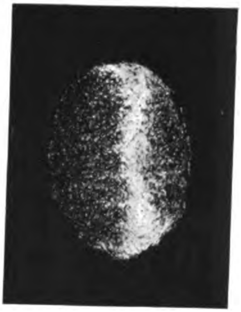


FIG. 20.

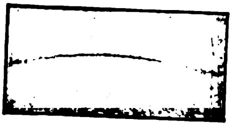


FIG. 23.

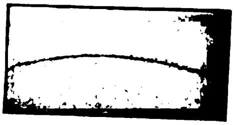


FIG. 24.

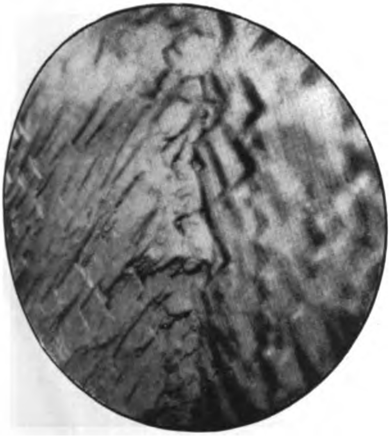


FIG. 33.

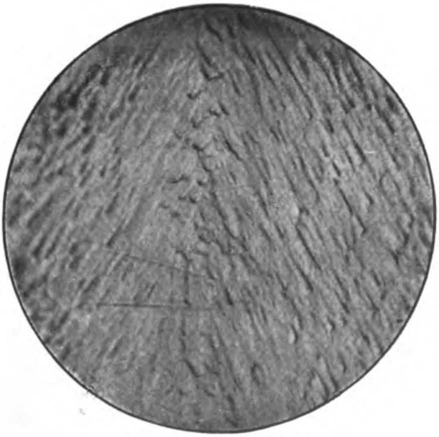


FIG. 34.

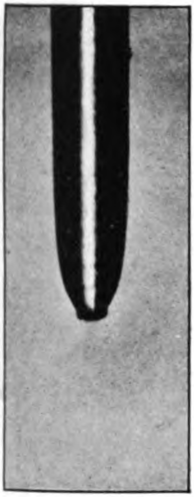


FIG. 17.

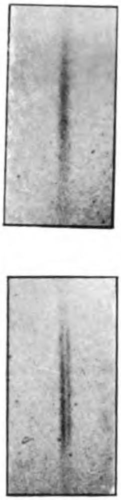


FIG. 28.

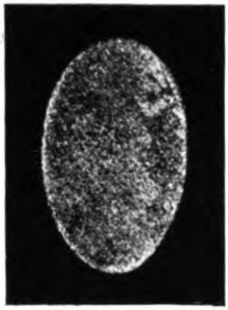


FIG. 21.

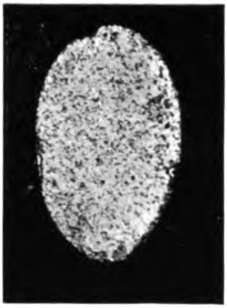


FIG. 22.

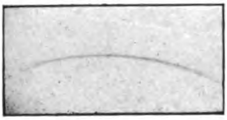


FIG. 25.

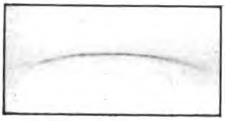


FIG. 26.

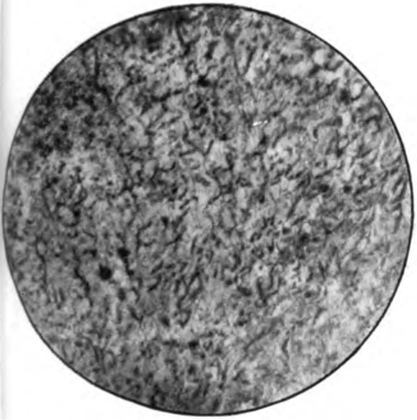


FIG. 35.

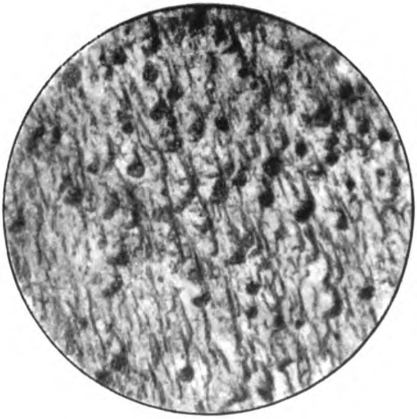
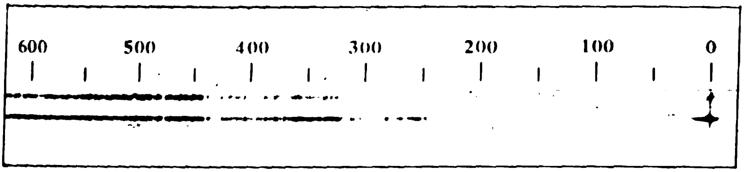


FIG. 36.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

AUGUST 1926.

XXVII. *The Effect of Tension on certain Elastic Properties of Wires.* *By* E. EDWARDS, *M.A.*, *B.Sc.*, I. BOWEN, *M.Sc.*, *and* S. ALTY, *M.Sc.*[*]

[Plate VII.]

AN increase in the torsional stiffness of phosphor-bronze strips as the result of increased tensions was investigated by Pealing[†]. In the experiments to be described the phenomenon was further examined with the view to seeing, if possible, the nature of the mechanism involved. In the first part of the work the dynamical method was applied, and considerably more light was thrown on the effect. The variation of stiffness was found to be present in all the wires tested, although the amount of change depended on the crystalline condition of the material. An investigation of the amount of damping for torsional vibrations established the additional fact that it was reduced as tension was increased. A statical method was then evolved in which observations could be obtained more readily and with greater accuracy. This was applied to test-materials which were considered to possess a simpler internal structure—tungsten wire consisting of a single crystal in the first instance, and quartz filament, presumably non-crystalline, in the second instance.

These experiments seemed to show that the phenomenon depended on the structure of the material being partly crystalline and partly amorphous.

---

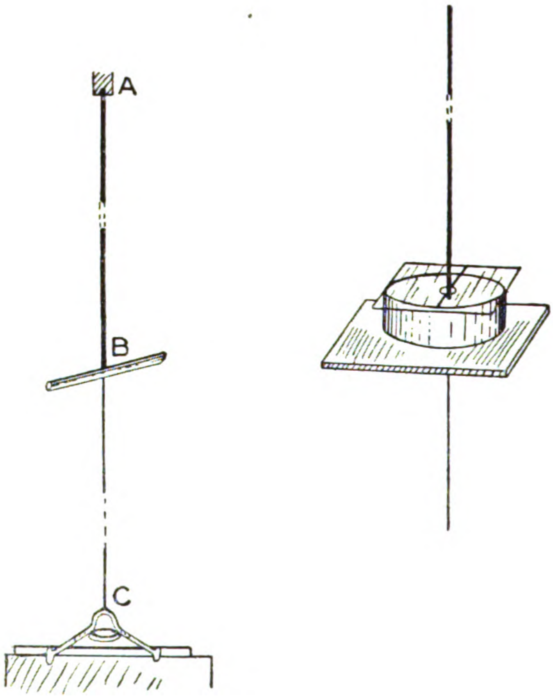
[*] Communicated by Prof. L. R. Wilberforce, M.A.

[†] Pealing, Phil. Mag. (ser. 6) vol. xxv. no. 147 (March 1913).

Dynamical Observations by I. Bowen, M.Sc., sometime Oliver Lodge Fellow.

Before proceeding on fresh lines the work of Pealing[*] was in part repeated, and the curves he obtained verified. His experiments had been performed by observing the oscillations of suspended bars of varying mass and inertia, and so calculating the torsional stiffness of the suspending phosphor-bronze strip for each case.

Fig. 1.



In the first part of the work recorded here, the change in moment of inertia of the suspended system was eliminated by use of the apparatus shown in fig. 1.

An oscillating bar B having moment of inertia large enough to give easily measurable period, but having small mass, was soldered to the end of a phosphor-bronze test strip AB, whose dimensions are given in the table of observations. From the point of suspension of this horizontal bar hung a fine unspun silk fibre BC, which could carry loads up to about 60 grms. The upper end A of the test strip or filament was clamped firmly in a vice, and to the end C of the silk fibre was attached a very light aluminium scale-pan. The masses of the inertia bar B and scale-pan C were kept small so that the suspension could be tested under a tension as small as 0·7 grm.

---

[*] *Loc. cit.*

In earlier experiments a vane consisting of a weighted metal box which just floated in glycerine (at a depth sufficient to leave only an attached scale-pan unimmersed) was used to prevent any rotation of the scale-pan; and the silk fibre BC was ascertained to have torsional stiffness small enough not to affect appreciably the period of oscillation of the strip and inertia bar AB.

A load varying from 0·7 to 60 grms. could thus be applied to the test strip AB and its period of oscillation determined, while the inertia of the system remained constant.

In later experiments the vane and glycerine were for convenience replaced by an aluminium scale-pan bearing two rigid projecting arms which hung between two vertical glass plates whose distance apart allowed the minimum of freedom to the arms.

This arrangement, as seen in fig. 1, allowed no rotation of the scale-pan, and at the same time the absence of friction at the glass surfaces permitted of the total load being applied to the test strip.

The results of experiments with this apparatus are expressed by the typical Curves I, where ordinates give $\frac{1}{T^2}$, T being the period of oscillation of the phosphor-bronze strip of length about 25 cm., breadth 0·054 cm., and thickness 0·0035 cm., and are proportional to the rigidity; while abscissæ give the tensions of the suspending strip measured in grammes. It will be seen that the torsional stiffness of the suspension increases with the load until at a certain value the rigidity becomes constant, and remains constant as the load is further increased.

In order to vary the conditions of the experiment, the silk fibre and scale-pan were replaced by a set of inertia bars of different moments of inertia and masses. Two pairs of bars were of equal mass but widely different inertia. Bars 5, 6 and 7, 8 form two such pairs. Thus taking one pair, the period of oscillation on a given suspension would be different for the two members; while their equal masses would cause the torsional stiffness of the suspension to be the same for both, provided the stiffness was dependent on tension alone, and not on period of oscillation. Results showed that the torsional stiffness depended only on the load applied.

The masses and moments of inertia of the bars are given in Table A below, with corresponding observations on the period. Curve II is derived from this table.

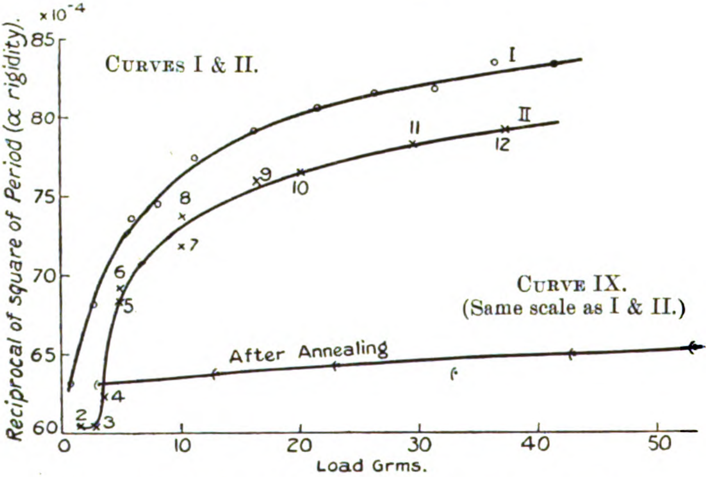


TABLE A.—Phosphor-Bronze Strip as Suspension.

Length 29·2 cm. Breadth 0·054 cm. Thickness 0·0035 cm.

The weight and moment of the wire cradle supporting the bars are included in the figures given in the second and third columns respectively.

Bar.	Tension, grms.	Moment of Inertia, grm./cm.²	Period of Swing.	Torsional Stiffness.
1	0·625	4·30	4·90	7·02
2	1·43	8·72	7·41	6·23
3	2·76	22·00	11·8	6·23
4	3·49	48·85	17·4	6·35
5	4·90	150·32	29·6	6·76
6	4·90	13·17	8·70	6·81
7	10·20	72·25	20·2	7·00
8	10·29	136·19	27·5	7·13
9	16·09	295·4	40·0	7·29
10	19·65	259·0	37·4	7·33
11	28·65	254·3	36·6	7·47
12	36·77	545·6	53·4	7·55

The loads were not quite large enough to reach the horizontal part of the curve.

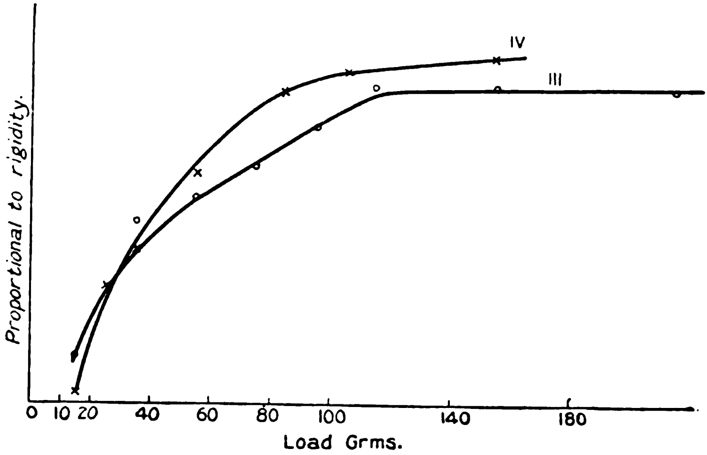
The fifth column in the above table gives values of the torsional stiffness τ of the suspension, τ being related to the period of oscillation T by the equation

$$T = 2\pi\sqrt{\frac{I}{\tau}},$$

where I is the moment of inertia of the suspended system about the axis of swing. It will be seen that the curve resembles those obtained by the previous method, and demonstrates the independence of τ and T since for bars of equal mass the values of τ are approximately equal, although the moments of inertia vary greatly.

In his researches Pealing failed to discover a variation of rigidity in wires having circular cross-section, and was led by this amongst other reasons to regard the variation in strips as being not a true change in rigidity but a change in torsional stiffness due to the effect of rolling in manufacture.

Curves III & IV.



The search for the effect in phosphor-bronze wires (the term "wire" being used here to imply circular section) was therefore of importance, since a wire drawn through a die-plate receives equal treatment over all parts of its surface; while the rolling of strips might overstrain one side of the material more than the other, in the manner suggested by Pealing. In other words, evidence of the variation in wires would lend support to the view that the phenomenon is not anomalous, but a true variation of rigidity.

The variation was found by the writer in phosphor-bronze wires, the specimens being supplied by Messrs. Johnson & Matthey. Curve III is drawn from a series of observations on the wire by the use of a scale-pan and glass plates described earlier in this paper. The maximum load applied in this case was 200 grms.

(It might be well to state here that decreasing loads were tried in these experiments, and the curves would always repeat themselves; in fact this procedure was always used as a proof that suspensions had not suffered overstrain under the maximum tension.)

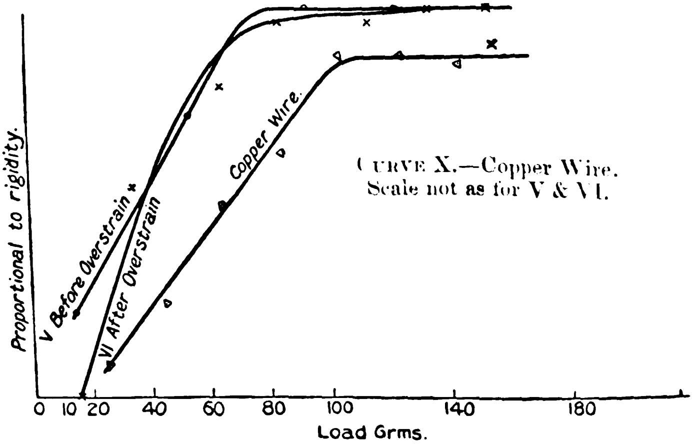
The period of 400 complete oscillations was determined to give each value.

Curve IV represents a series of readings on another piece of wire.

It is justifiable to assume that the shape of cross-section is not a determining factor of the presence of variation in torsional stiffness, for the curves give the same evidence of maximum rigidity as before. The wire had a diameter of 0·04 cm. and length about 35 cm.

The effect of overstrain, which had been thought by previous workers to produce the variation in rigidity, was next ascertained. A piece of the phosphor-bronze wire described in the last paragraph was loaded gradually until it was found to break under a load of 11·2 kilograms. A fresh unstrained piece was now submitted to oscillation tests, then overstrained till it "flowed" under a tension of 9·6 kilograms, and again tested for rigidity variation.

Curves V & VI. Drawn to same scale.

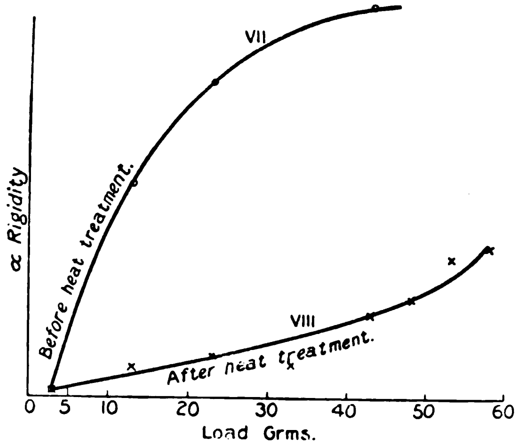


Curve X.—Copper Wire. Scale not as for V & VI.

Curves V and VI show the variation in rigidity before and after overstrain. The variation is still present, and the turning-point of the curves occurs for the same value of tension, roughly 100 grms. The variation does not disappear when the material is overstrained.

In order to examine the effect of heat treatment on the rigidity variation, a furnace was built of a glazed porcelain tube measuring 30 cm. in length and having an internal diameter of 3 cm. Around this tube was wound a solenoid of nickel-chromium alloy resistance-wire capable of giving a temperature of 2000° C. with a current of 7 amps. The windings were about 2 mm. apart, being closer at the ends where cooling might be considerable. The whole was enclosed in a plaster of alundum powder mixed with sodium silicate and wrapped with asbestos cord and sheeting to form a thick coating. A small vice at one end of the tube held one end of the wire undergoing treatment, the other end being held taut outside the surface by a weak spiral spring. Since phosphor-bronze oxidized rather readily at high temperatures, a copious supply of hydrogen was kept flowing through the furnace. A platinum resistance thermometer in conjunction with a Callendar-Griffiths bridge gave temperature readings.

Curves VII & VIII. Drawn to same scale.



For 30 minutes a phosphor-bronze strip, whose rigidity had been examined in the usual way, was maintained in the furnace at a temperature of 350° C. After slow cooling, the part of the strip which had been inside the furnace was again tested. The material had become soft and less springy, indicating that annealing had taken place to some extent. The results of the tests before and after heating are given by Curves VII and VIII.

There appeared a decrease in the rigidity variation amounting to about 70 per cent., while after heat treatment no turning-point, at which rigidity ceases to increase with load, was apparent, even though the load applied reached 60 grms.; whereas before heating a turning-point occurred between 20 and 30 grms. Several strips were examined after heating to 400° C., and the variation in torsional stiffness was always present though much reduced.

Microscopic examination of the effects of heat treatment on the metal was next attempted. Specimens 1·5 cm. in length were mounted in sealing-wax and polished, with a polish-etch of magnesium oxide in ammonia to which had been added a few drops of hydrogen peroxide. The difficulties of handling such fine specimens need not be described here. Photographs of specimens so prepared taken under "normal illumination" are shown in Plate VII. In the unheated specimens of phosphor-bronze the crystals were seen to be much elongated due to cold rolling in the manufacturing process. The crystals were all of the same composition, a solid solution or binary alloy of the two constituent metals which had remained unchanged by the process of solidification.

Examination of the specimen which gave Curve VIII after heating to 350° C. showed the development of small "incipient" crystals as new centres of recrystallization. To obtain more complete recrystallization a length of the strip was heated in the furnace to 730° C. and maintained so for an hour, when it was slowly allowed to cool. A rigidity test on this specimen yielded Curve IX. The variation was still present after this complete annealing (shown by the second photograph on the plate) and formation of large crystals. Again the curve showed no turning-point corresponding to the attainment of a maximum rigidity.

Thus annealing lessened the variation, the decrease being greatest for most complete annealing, or formation of largest crystals, while the turning-point disappears from the curves.

Lack of time prevented the working of a complete set of data for drawn copper wire, but it is noteworthy that the same variation and turning-point was discovered in copper. Curve X shows the variation in rigidity of a drawn copper wire 0·033 cm. in diameter.

Partial annealing was again found to lessen the variation. The experiments so far described led to the idea that the variation in rigidity was caused by some internal mechanism in the crystals of the metal. The simplest explanation seemed to be that of slip within the crystals. Should a crystal be deformed by slip along a slip-plane, then, provided the deformation be slight, any disturbed molecules in the plane of slip would be able to rearrange themselves pretty much in their original way, crystal orientations and integrity being thus restored. Excessive slip would produce permanent disturbance in a slip-plane, while excessive alternating strains tend to produce an amorphous layer in the slip-plane, giving rise to "fatigue" *.

In the experiments described here, the deformation was slight enough to permit of rearrangement of the disturbed molecules. The individual crystals of a metal are, according to Rosenhain, surrounded by an intercrystalline cement of amorphous metal, and recent work goes to show that this amorphous metal possesses greater strength than the crystal itself, slip-bands occurring in such a way as to produce least disturbance of this cement.

Thus in a strip of phosphor-bronze we have a large number of crystals bound together by a three-dimensional network of strong amorphous metal. When the strip or wire is under tension, the intercrystalline cement binds tightly on the crystals and prevents their internal slipping ; while under sufficient tension this binding effect may be great enough to prevent any slip in the crystal, rigidity then remaining constant in spite of further increase in tension.

When crystals are small, as before heat-treatment, the binding effect of the amorphous cement is more pronounced and the maximum rigidity is reached for a smaller load than is necessary when crystals are large. This would account for the absence of a turning-point in the rigidity curves for annealed specimens.

To test this theory a series of experiments was carried out on the internal damping of oscillations in phosphor-bronze suspensions. Damping should be great when internal slip is great; while the damping would reach a minimum when slip ceased and rigidity became maximum and unvarying, that is to say, for large loads. The following experiments bore out this prediction.

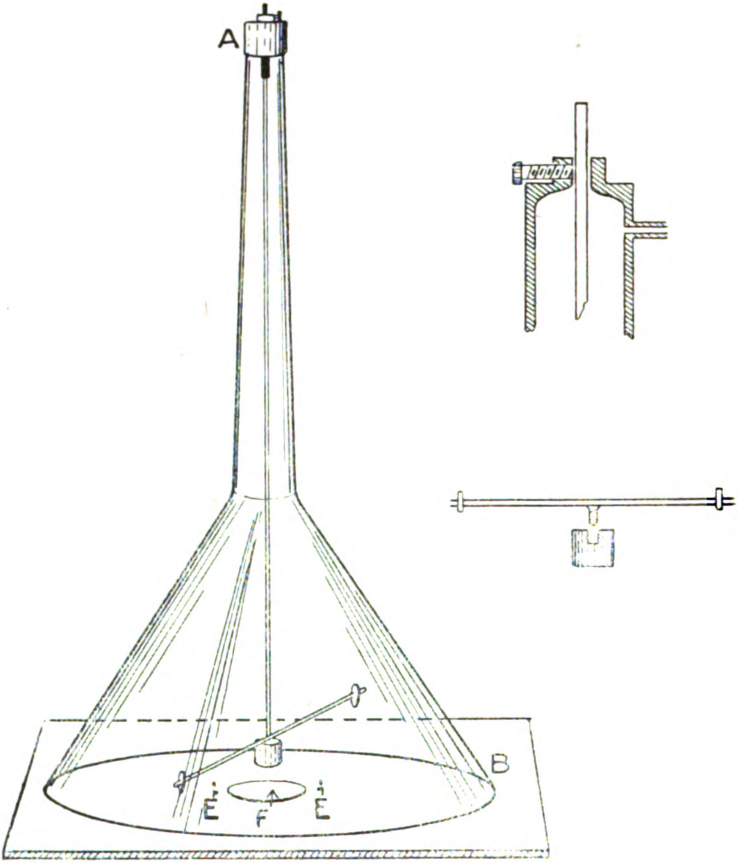
In fig. 2 is sketched the apparatus, consisting of a large filter funnel ground to fit closely on to a stout metal base B. On the small end A of the funnel was fitted a cap having an exhausting tube and a clamp which allowed a stout rod to pass through (as shown in the smaller diagram). To the lower end of this rod was soldered the phosphor-bronze suspension. In these damping experiments it was desirable

---

* Ewing and Humphrey, Phil. Trans. Roy. Soc. A, cc. (1902).

to keep the period of swing constant, and so overcome variations due to air-friction. The different loads applied were therefore constructed to have equal moments of inertia, and to screw on to the light inertia bar as in fig. 2. Any slight inequality in moment of inertia could be compensated by adjusting the positions of the two small iron disks on the inertia bar, while the suspended system could be set oscillating by means of an electromagnet held outside the chamber to attract either of these disks. The apparatus was exhausted to reduce variation due to air-friction or viscosity when the different shaped loads were applied.

Fig. 2.



A removable plug F in the base-plate facilitated the changing of the loads, small hooks E in the base serving to hold the inertia bar steady during the operation.

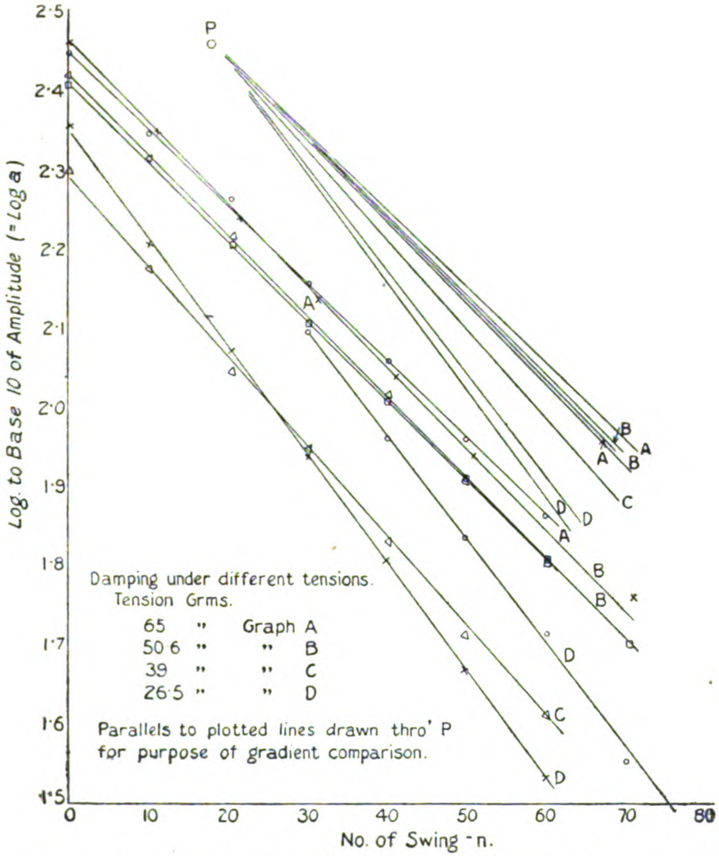
The sliding bar in the cap A permitted the lowering of the suspension for changing the load. All joints were made air-tight with wax. A scale penned on the glass wall of the funnel at its base gave amplitude readings.

If r be the ratio of two successive amplitudes to one side, and $a_0, a_1, a_2, \ldots a_n$ the amplitudes of the 1st, 2nd, 3rd and (nth + 1) swings to the same side, then

$$r^n = a_0/a_n$$

and
$$\log r = \frac{\log a_0 - \log a_n}{n}$$

Graphs XI.



Thus if the damping has been uniform through a set of oscillations, a graph giving values of n as abscissæ and corresponding values of $\log a_n$ as ordinates should be a straight line, as shown by graphs XI. Each line in this set was obtained as the result of several damping tests for a particular load. It is clearly seen that the coefficient of damping decreases as tension and rigidity increase, while there is a limit to the damping as there is to rigidity, both limits occurring for about the same value of tension. These experiments on damping therefore support the theory suggested to explain the variation in rigidity.

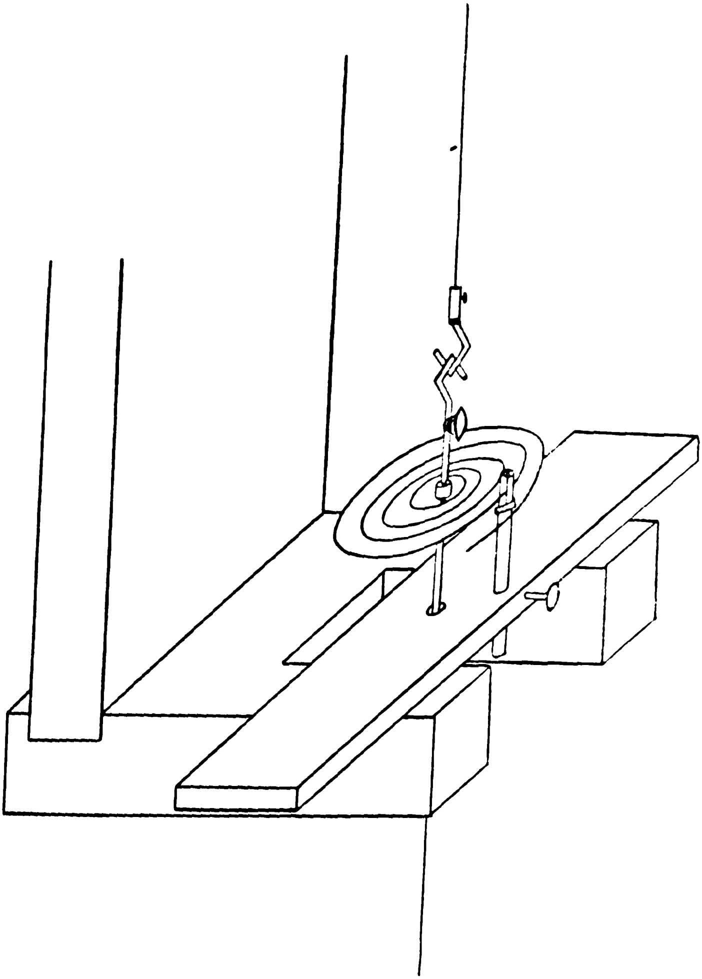
Statical Measurements by S. Alty, M.Sc.

Experiments of a statical nature were carried out to investigate further the variation of stiffness of strips and wires with load. The method and apparatus used were somewhat similar to those described in Searle's 'Experimental Elasticity,' p. 155, in connexion with torsional hysteresis.

The upper end of the wire was clamped to a torsion-head graduated to read tenths of degrees, and the lower end was attached to a flat spiral spring of suitable strength, the outer end of this spring being clamped to the framework. Changes in the strength of this spring were easily made by altering the part of the spring engaged in the framework-clamp, and so varying the length of the spring. As can be seen in fig. 1 *a*, the attachment to the spiral spring is made through two hooks of square cross-section to provide geometrical contact for the transmission of couples. This provision made the substitution of wires an easy matter. The tension is governed by the weight which is attached below the stand. The method of procedure was to produce a twist of known amount by the torsion-head, causing the lower end to turn through a small angle in opposition to the controlling spring. This angle of rotation was measured by means of a mirror fixed to the central wire. The couple acting was proportional to this angle. Hence we got a measure of the couple corresponding to any twist produced.

As the tensions were produced by attaching weights to the wire below the spiral spring, a complication entered due to the rotation of the wire at its lower end. If the scale-pan carrying the weights was free, then this rotation when produced caused the scale-pan to vibrate torsionally, and this vibration would upset the reading obtained from the mirror. There were two ways of overcoming this difficulty in theory. The first would be to prevent any rotation of the scale-pan and to interpose some very fine suspension between the spiral spring and the scale-pan to eliminate any controlling effect on the twist of the spiral spring and wire. At best, this would leave a slight residual controlling effect and the reading obtained for the twist of the lower end of the wire would be slightly reduced on that account.

Fig. 1 *a*.



The way adopted, therefore, was to turn the scale-pan by hand through an angle equal to the rotation of the wire at the spiral spring. In this way the twist in the suspension from spring to pan was maintained zero. This method worked very satisfactorily.

The order of procedure in an experiment was as follows :—

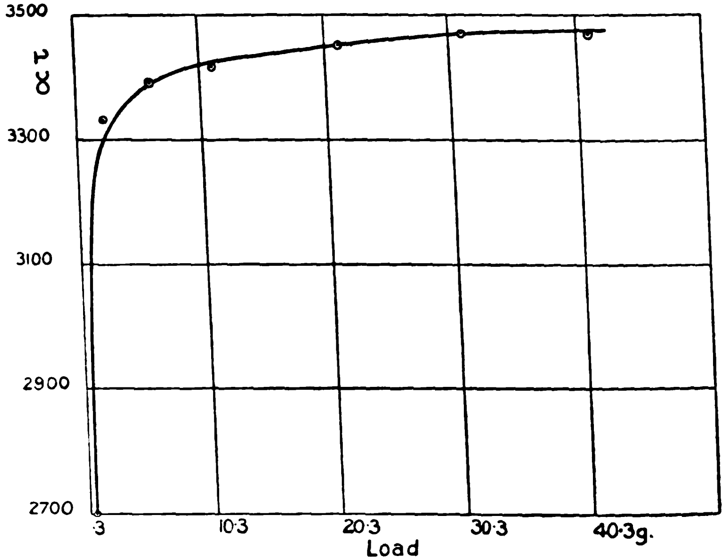
The wire was attached to the torsion-head, spiral spring, and scale-pan. All control was removed by unclamping the framework end of the hair-spring and allowing the scale-pan to be quite free. The mirror readings at spiral spring and scale-pan were noted, the outer end of spring was now clamped, the torsion-head was turned through an angle θ_1°, and the deflexion θ_2° for the lower end observed on the scale. The scale-pan was then turned through an angle equal to this, or rather slightly more because, as the scale-pan is turned, θ_2 increases slightly.

Then the total twist in the wire $= \theta_1 - \theta_2$, and the couple G is proportional to θ_2.

$\frac{G}{\theta}$, which measures the stiffness, is therefore proportional to $\frac{\theta_2}{\theta_1 - \theta_2}$.

Measurements were made of these angles for a series of loads for each wire or strip tried, using in each case various values of angles. The results were shown graphically by plotting the value of θ_2 against the corresponding value of $\theta_1 - \theta_2$.

Fig. 2 *a*.



Phosphor Bronze.

With phosphor-bronze strips, the first material to be tried, a variation in the stiffness of the same general character was obtained with all, but the amount of the change varied from 5 per cent. to 35 per cent. in different specimens.

The curve shown in fig. 2 *a* is typical of the effect obtained

These results agreed in a general way with those that had been obtained by the dynamical method of Mr. Bowen.

As the phenomenon had already been shown to be connected with the internal structure of the metal, it was desirable to test specimens of known internal structure, and possibly, in that way, gain some knowledge of the mechanism involved.

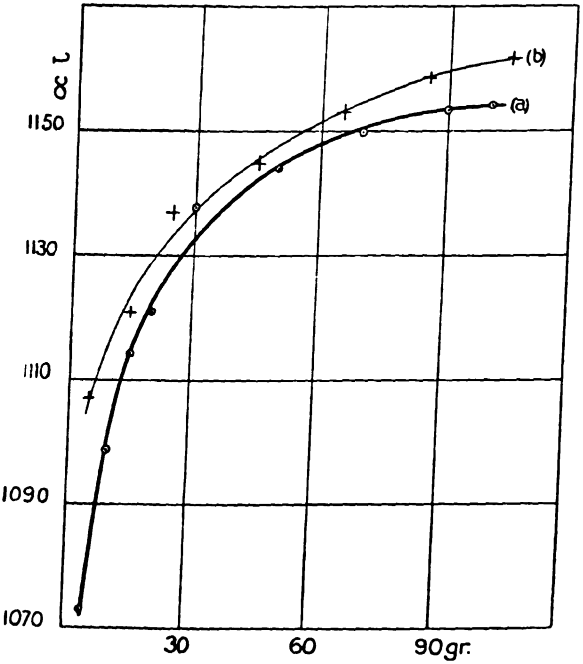
Tungsten.

Through the kindness of the General Electric Company, lengths of tungsten wire and of Pintsch single crystal wire were obtained and tested by the above method.

The diameter of the wire was ·20 mm.

The hair-spring used for the phosphor-bronze strips was replaced by a much stronger one, and the effect due to the stiffness of the thread between spiral spring and scale-pan became inappreciable. In all other respects the apparatus was unaltered.

Fig. 3 *a*.

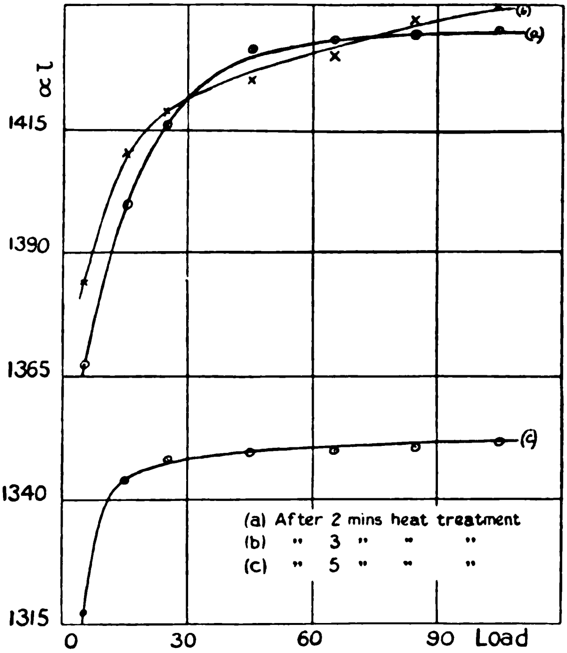


The results of the experiment on the ordinary drawn tungsten wire are shown in fig. 3 *a*, curve (*a*), the curve being of the usual type and the percentage increase in stiffness being 7·46 per cent. between loads of 5 and 105 g.

In the drawn wire there will be a large number of crystals occupying any one cross-section. The Research Staff of the G.E.C. have carried out experiments * on the properties of "recrystallized" tungsten wire. In this the crystals will have grown, and if the recrystallization is complete then many of the crystals will fill completely the cross-section of the wire.

With the view to finding how the change of stiffness varied with the size of the crystals, the stiffness experiment was carried out on the ordinary drawn wire at stages of increasing recrystallization.

Fig. 4 *a*.

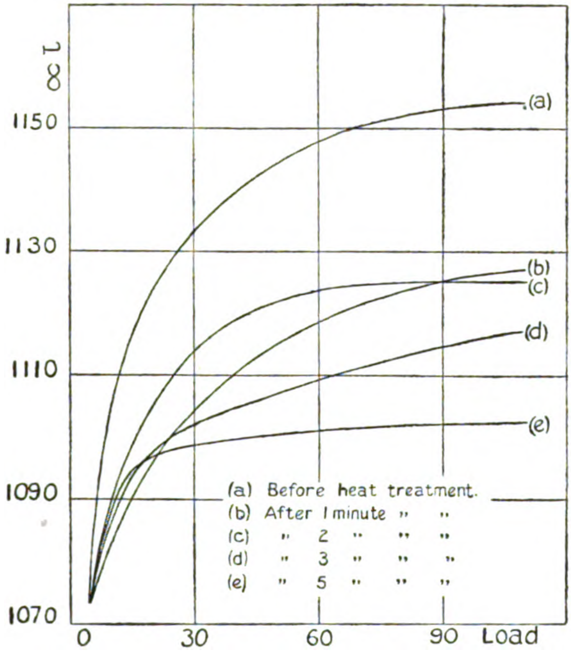


As the recrystallized wire was extremely brittle, it was necessary to carry out the process *in situ*. To do this the wire and the hook attached to it were enclosed in a glass tube fitting on to a stopper which was attached to the torsion-head. The hook supported a small cup of mercury, this giving good electrical contact, and exerting sufficient tension on the wire to hold it taut. Recrystallization was brought about by raising the wire to a white heat in an atmosphere of hydrogen, the current necessary being led in by mercury connexions and a platinum contact at the bottom of the tube. The current was passed through the wire for one minute, the tube removed, the spring hook replaced on the other, and the experiment repeated. This was done four times on the supposition that the crystals would become larger each time, and the results are shown in figs. 3 *a*, 4 *a*, and 5 *a*, the change in stiffness becoming less. In fig. 5 *a* the curves for the wire in all its stages are given the same value of stiffness for a load of 5 g., and the scale of each curve suitably reduced for ease of comparison.

---

* Phil. Mag. Aug. & Nov. 1924.

Fig. 5 *a*.



The Pintsch tungsten wire, which consisted entirely of a single crystal, was next tested and was found to show no variation, the torsional stiffness being independent of the load. The largest discrepancy was less than 1 per cent., and was considered to be due to the fact that for loads of less than 10 g. the wire was not taut. There was no indication of a regular variation with load.

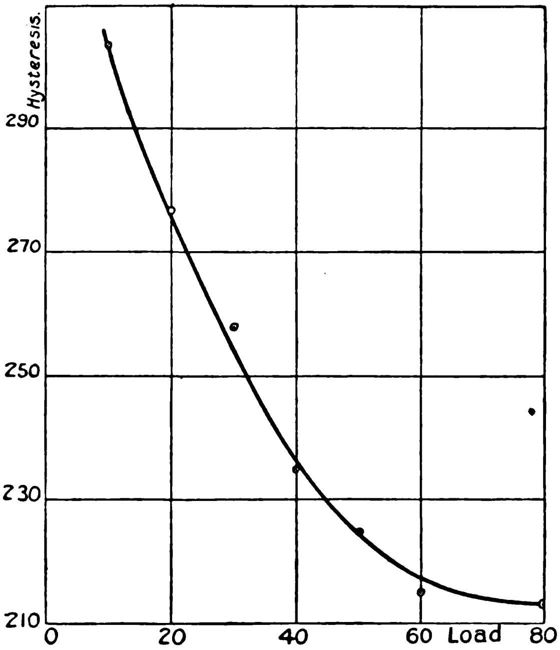
Quartz Fibre.

The experiment was also carried out using a quartz fibre, this having no crystalline structure, and it was found that the stiffness was quite independent of the load.

Variation of Hysteresis of Wires with Load.

On carrying out the usual hysteresis experiments for the drawn tungsten wire, it was found that the hysteresis loop was too narrow and indistinct to be of use in showing in what way, if any, the amount of hysteresis varied with load. An indication of the hysteresis for different loads was found as follows :—With the wire originally free from twist, the torsion-head was turned through 360° in a clockwise direction and then back to zero. The spot of light reflected from the mirror attached to the hair-spring was observed to have been deflected in a counter-clockwise direction, and its new position was noted. On turning the head through 360° in a counter-clockwise direction and back to zero the spot of light shifted in the opposite direction, and its reading was

Fig. 6 *a*.



again observed. The difference between the two readings was proportional to the amount of slip which had occurred in the wire during the two twists. The difference between these readings may be taken as an indication of the amount of hysteresis.

It was necessary to bring back the torsion-head accurately to zero, since a small error here would have rendered the scale-readings useless. To do this a mirror was attached to the head and a scale set up at a distance of 1 m. from the mirror. The torsion-head was turned so that the spot of light returned to the same point on this scale each time, thus ensuring that the head was always brought to the same zero. In this way a measure of the hysteresis was obtained for a series of loads.

The Pintsch single crystal wire showed practically no variation of hysteresis with load, there being slight irregularities for loads less than 10 g. due probably to the fact that the wire was not taut. For loads above 10 g. the hysteresis was constant.

The results obtained for the drawn tungsten wire are shown in fig. 6 *a*. In this case the hysteresis varies greatly with load, assuming a minimum value at a load of about 75 g., and remaining unchanged for loads of higher values

THE YOUNG'S MODULUS OF WIRES FOR SMALL TENSION.

In view of the general variation of torsional stiffness, it was considered desirable to examine the stretching of wires by small tensions. The great difficulty in this investigation was to ensure the absence of spurious effects due to the straightening out of small irregularities. When this had been overcome, it was observed that the ratio of increase of length to the stretching force was much greater for the smallest forces employed than for larger ones. This has been observed with copper and iron wires of about 1 mm. diameter, the change disappearing for tensions of the order of 100 grms. The work has not proceeded far enough for publication at present, but it is hoped that the results for a number of different materials together with an account of the method and apparatus employed will be completed shortly.

CONCLUSIONS.

One fact seems to be well established—that the observed changes in the elastic properties of materials depends on their structure being partly amorphous and partly crystalline, and that they are most marked when the crystals are small, a condition produced by any hardening process. From the elementary theory, it can be seen that the stress due to a tension may be regarded as equivalent to a hydrostatic negative pressure (an outward pull on all parts of a surface) together with two shearing stresses in two perpendicular planes, both of which pass through the axis of the wire. Of these, it seems reasonable to consider the first as responsible for the observed effect, in so far as it involves a change in volume of any element, which implies an increase in the separation of the molecules.

The condition seems to be analogous to a chain composed of a large number of links, but in our case we have a network of links, in three dimensions; under small tensions there is a looseness in the linking together of neighbouring elements, while increase of tension by separating these elements slightly, increases the strength of the bonds existing between them.

Other experiments have shown that slip occurs readily in crystals along certain planes. The fact that a wire of one crystal does not exhibit any variation, tends to lead to the view that the crystals in the interior of a multicrystalline material are not in the same condition as would be found in the case of a single large crystal. This difference must be caused by the intercrystalline amorphous material or cement as it is commonly called. A hydrostatic pressure on the crystals might conceivably account for the effect, provided such a pressure resulted in greater freedom of slip within the crystals, and an experiment to test this point is being contemplated. If that could be established as a fact, the mechanism involved in the increase of stiffness and decrease of damping and hysteresis would be fairly clear. The increase in volume brought about would relieve the pressure on the crystals, and they would exhibit properties similar to those of single large crystals with free surfaces.

In conclusion, the authors wish to express their thanks to Prof. L. R. Wilberforce for suggesting the work, to Prof. C. O. Bannister for placing the resources of the Metallurgy Department both as regards equipment and advice at our disposal for getting the photo-micrographs, and to the General Electric Company for their kindness in allowing us to have a length of their single crystal tungsten wire.

XXVIII. *The Surface Tension of Liquid Metals.*—Part I. *Tin and Lead.* *By* L. L. Bircumshaw, *B.A.*, *M.Sc.* (*from the National Physical Laboratory*) *.

THE surface tension of molten metals was the subject of experimental study by Quincke † as long ago as 1868. In this paper and in one ‡ which appeared in the following year, determinations of this constant were made by a somewhat crude application of the drop-weight method, viz. the weight of the drops which fell from a melting wire of known diameter was determined. The difficulty of controlling the formation of the drops and the great uncertainty of the circumference from which the drop falls render this method little more than qualitative. In later papers § by the same author the capillary constants were deduced from measurements of the dimensions of a drop of the molten metal resting on a plane surface. Siedentopf ‖ in 1897 published a paper containing the results of a large number of determinations by this method, and it has also been used by Heydweiller ¶ and by Gradenwitz **, while Grünmach †† used the method of ripples. Smith ‡‡ measured the capillary depression of the metal in a carbon tube, using a micrometer depth gauge and an electrical device, and gives results for mercury (15°–17°), bismuth (700°–850°), antimony (840°–850°), lead (770°–780°), tin (750°–910°) aluminium (700°–820°), zinc (580°–630°), silver (980°–1120°), gold (1120°), and copper (1150°). In this work, however, the angle of contact was assumed to approach 180°, so that in all probability most of these results will be low.

The most important work on this subject during recent years is due to Hogness §§, who used the method of "maximum bubble pressure." He measured the excess pressure developed in a small bubble of the metal when forced from the end of a fused silica tube of known radius, and determined in this manner the surface tension of mercury (up to the boiling-point) and of tin, lead, bismuth, cadmium, and zinc up to 500°. The theory of the method of maximum bubble pressure was first described by Cantor [*], and subsequently by Feustel [†], Ferguson [‡], and Schroedinger [§], who gives the formula

---

* Communicated by Walter Rosenhain, B.A., D.Sc., F.R.S.

† Poggendorf's *Annalen*, cxxxiv. p. 356 (1868).

‡ Poggendorf's *Annalen*, cxxxv. p. 261 (1869).

§ Poggendorf's *Annalen*, cxxxviii. p. 141 (1870); cxxxix. p. 1 (1871).

‖ *Ann. d. Physik*, lxi. p. 235 (1897).

¶ *Ann. d. Physik*, lxii. p. 694 (1897); lxv. p. 311 (1898).

** *Ann. d. Physik*, lxvii. p. 467 (1899).

†† *Ann. d. Physik*, iii. p. 660 (1900).

‡‡ Journ. Inst. Met. xii. p. 168 (1914).

§§ Journ. Amer. Chem. Soc. xliii. p. 1621 (1921).

$$a^2 = rh\left(1 - \frac{2}{3}\frac{r}{h} - \frac{1}{6}\frac{r^2}{h^2}\right).$$

Here a^2 is the specific cohesion, r the radius of the tube, and h is the maximum pressure in the bubble expressed in centimetres of the liquid itself. This formula obviously only holds when $\frac{r}{h}$ is small, but a complete numerical solution of the differential equations involved is given by Bashforth and Adams [‖]. Sugden [¶] in a valuable paper has dealt with the theory of this method and utilized Bashforth and Adams's tables to calculate values of the complete correction $\frac{X}{r}$ in the equation $a^2 = rh \cdot \frac{X}{r}$, and gives a table of values of $\frac{X}{r}$ for a range of $\frac{r}{a}$ from 0·0 to 1·5. In the present work it was decided to use the method of maximum bubble pressure, as it possesses two great advantages: it is independent of the angle of contact, values of which in the case of liquid metals are almost always unknown, and a new surface of the metal is blown in each separate determination.

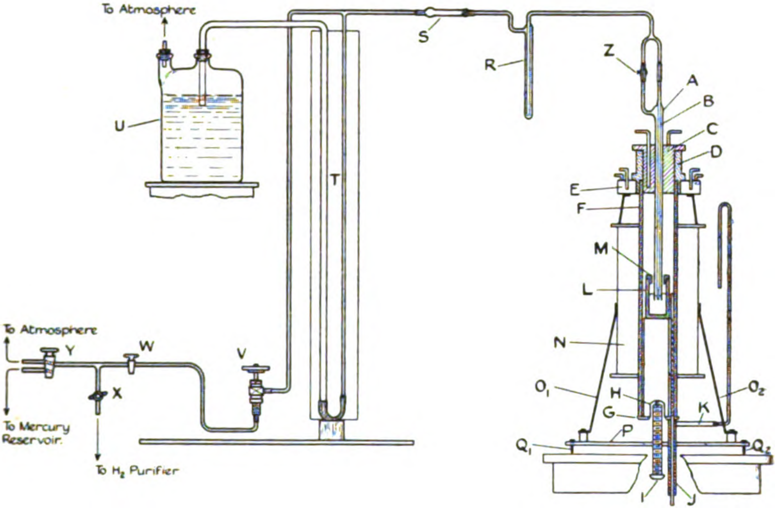
Experimental.

The apparatus is shown diagramatically in fig. 1, and consists of a fused silica tube A, 42 cm. long, 1·12 cm. external diameter, and 0·92 cm. internal diameter, into which is fused a second silica tube B about 0·4 cm. diameter. This tube has been drawn down and the ends of both tubes have been ground, so that the cross-section of each is in the same plane. The diameter of the tube has been measured in two directions at right angles in the Metrology Department of the National Physical Laboratory, and the measurements were found to differ by 1 per cent., the mean diameter being 1·016 cm. The tube A fits closely through a hollow water-cooled brass plug C, which in turn fits into the brass collar D; E is a copper water-cooler placed in close contact with the lower half of the latter. The silica furnace tube F at its lower end is closed by a brass plate G fitted with a central cone H, into which passes the screw I, and soldered into this plate is a brass tube J, through which passes the silica couple tube. Another brass tube K is soldered into J, to the end of which is attached a glass tube (2–3 mm. in diameter) which serves as a gas outlet from the furnace.

---

[*] Wied. *Annalen*, xlvii. p. 399 (1892).
[†] Drud. *Annalen*, xvi. p. 6 (1905).
[‡] Phil. Mag. vi. p. 128 (1914).
[§] *Ann. d. Physik*, xlvi. p. 413 (1915).
[‖] 'Capillary Action,' Cambridge, 1883.
[¶] Trans. Chem. Soc. cxxi. p. 858 (1922).

Fig. 1.



On the plate G rests a Mabor cylinder, which supports an alundum crucible L which contains the metal, and a clay cover M fits the top of the crucible. The furnace-tube is wound with nichrome wire and the case N is held by three steel stays O_1 O_2 O_3, which are screwed down to the base P, the latter being supported on the table by three levelling screws Q_1 Q_2 Q_3. After the tube A had been fitted through the plug C and held firmly in position by means of a little pitch on the top surface of the plug (a film of wax was also placed between A and the inside wall of the cooler), the lower ends of the two tubes were very carefully ground so that their cross-section lay in the same plane, and this plane was parallel to the machined top of C. In order to ensure that the plane of cross-section of the tubes is horizontal, it is then only necessary to level up the top of C with a spirit-level, by means of the screws Q_1, etc. The joint between the furnace-tube and the plate G is made tight with a little clay, which is covered with a film of pitch. This has been found to be quite satisfactory. The tubes A and B are connected by means of pressure tubing, in the manner shown in the sketch, to a glass trap R immersed in solid CO_2 and acetone contained in a thermos flask, and the trap is connected through a drying tube S (loosely packed with calcium chloride) to the manometer T. One arm of the latter consists of a narrow tube 50 cm. long and 3 mm. diameter graduated in millimetres, which was carefully calibrated before being sealed into the apparatus. The wide arm is connected to a large Woolf bottle U 16 cm. in diameter and is open to the atmosphere. Water, coloured with a trace of potassium dichromate, was used as the manometric liquid, and no trouble due to the sticking of the meniscus was observed. The manometer is also connected through a valve V to the taps W, X, and Y.

To make a determination, a piece of metal of about the correct volume is turned up to fit loosely into the crucible and a cylindrical hollow cut in it, into which fits very loosely the end of the tube A. The joint at G is sealed and the junction between the plug C and the collar D waxed over. Hydrogen, generated electrolytically from 5 per cent. caustic soda (using iron electrodes), is passed over silica chips heated to 600° and dried over calcium chloride. The gas is then passed through the apparatus for two to three hours by closing Y and opening X and W, after which the furnace is heated until it has attained the desired constant temperature. Attached to the tap Y is a large gas burette, and by closing W this can be filled with gas from the generator, then by opening Y and W and closing X, bubbles can be blown by using the gas in the burette under a convenient pressure. The valve V enables the bubbles to be formed quite slowly. A determination consists in measuring the pressure required to liberate a bubble from the wide tube and the pressure required to liberate a bubble from the narrow tube, and from these observations the surface tension can be calculated. A screw clip is placed on the connecting rubber tubing at Z, and if this is open bubbles will blow from the wide tube, whereas if it is closed they will, of course, come from the narrow tube. When bubbles are blown from the latter, the pressure rises and the metal is depressed in the wide tube, which alters the hydrostatic head slightly. After each reading with the narrow tube therefore the pressure in the apparatus is carefully released (nearly to atmospheric) through the tap Y. After a determination when the metal is just above the melting-point, the seal at G is broken, and by means of the screw I the metal before it freezes is dropped just below the end of the tube A.

The results are calculated by the method given by Sugden (*loc. cit.* p. 861). If the two tubes of radius r_1 and r_2 respectively are immersed to a depth t cm., and h_1 and h_2 (in centimetres of the liquid) are the pressures required to liberate bubbles, then we have

$$h_1 = \frac{a^2}{X_1} + t \quad \text{and} \quad h_2 = \frac{a^2}{X_2} + t,$$

so that

$$H = h_1 - h_2 = a^2\left(\frac{1}{X_1} - \frac{1}{X_2}\right)$$

and

$$a^2 = \frac{H}{\dfrac{1}{X_1} - \dfrac{1}{X_2}}.$$

To calculate the first values of X_1 and X_2 for the result at the lowest temperature, the means of the values of a^2 given by Smith and by Hogness have been taken as approximate values, while in calculating the results for successively increasing temperatures the final value of a^2 for the previous temperature was taken. a^2 was then calculated by the method of successive approximations *. The above method of calculation can, of course, only be used when the level of the liquid is not sensibly altered by the volume occupied by either bubble, *i. e.*, theoretically when the surface of the liquid is an infinite plane. In the present case, where the metal is contained in a crucible 3·0 cm. diameter, this condition is far from being fulfilled, and a correction has to be made for the increase in the value of t, due to removal of metal from the tube and the volume occupied by the bubble. In the case of the narrow tube this was neglected, and in the case of the wide tube the method of correction can be illustrated by taking the case of tin at 253°. Taking $\gamma = 500$ dynes/cm., $a^2 = 0{\cdot}1460$ sq. cm., $a = 0{\cdot}3821$ cm., $\frac{r_2}{a} = 1{\cdot}466$ (r_2 is the radius of the wide tube and $= 0{\cdot}56$ cm.), $h = 15{\cdot}5$ cm. of water, and D^{250} for tin $= 6{\cdot}982$. From Sugden's table we find X_2 to be equal to $0{\cdot}2334$, hence $h = \frac{a^2}{X_2} + t$, where h is $2{\cdot}220$ cm. of Sn, we find $t = 1{\cdot}595$ cm. of Sn. We have then to determine the capillary depression in the wide tube.

---

* In certain cases values of X/r for $r/a=2·0$ approximately were required. The value of X/r for $r/a=1·8$ (which appears to be the highest value of r/a which Bashforth and Adams's tables enable us to deal with) was calculated and the curve extrapolated.

Now

$$2\gamma = rd\,hg \quad (r = 0{\cdot}46 \text{ cm.})$$

(for this correction term the angle of contact is taken as 180°), hence the height of metal in the tube is 1·278 cm. The volume of metal displaced will be

$$3{\cdot}142 \times (0{\cdot}46)^2 \times 1{\cdot}278 + \frac{\frac{4}{3} \times 3{\cdot}142 \times (0{\cdot}56)^3}{2} \text{ c.c.}$$

if the volume of the bubble is taken approximately as a hemisphere. This amounts to 1·218 c.c. The volume between the wide tube and the wall of the crucible amounted to 6·084 c.c. per centimetre height, so that the increase in t * amounts to 0·200 cm. As this increased height operates when a bubble is blown from the wide tube but not from the narrow one, it must be added to H.

The results, which are the means of a large number of determinations, are given in Table I. The pressures P are given in centimetres of water, and the densities have been taken from a paper by Day and Sosman †. The tin used contained at least 99·99 per cent. of that metal, and the lead contained only 0·002 per cent. of Cu and 0·002 per cent. of Fe.

---

* This is not quite exact. The value of t calculated in this manner is the depth of liquid after the metal has been displaced, and the capillary depression should strictly be subtracted from the original rather than from the final level. The error introduced in this way acts in the opposite direction to the error involved in taking the angle of contact as 180° in calculating the depression.

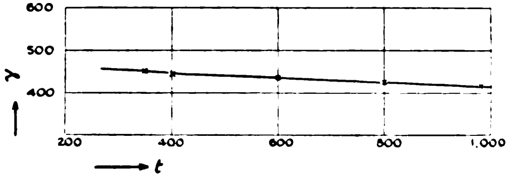
† Amer. Journ. Science, 1914, xxxvii. p. 10.

TABLE I.

Temp. °		P. Wide.	P. Narrow.	a^2 (cm.)^2.	γ dynes/cm.
			Mercury.		
19	....	14·4	26·7	·0708	470
			Tin.		
253	....	15·5	31·0	0·1538	526
299	....	15·5	31·05	0·1547	527.
401	....	15·55	31·05	0·1558	526
600	....	15·6	31·10	0·1584	525
800	....	15·6	30·95	0·1596	520
964	....	15·6	30·80	0·1601	514
			Lead.		
350	....	19·9	31·5	0·0865	453
402	....	20·0	31·4	0·0857	446
600	....	20·35	31·4	0·0858	436
800	....	20·5	31·2	0·0855	425
982	....	20·6	30·9	0·0850	414

The results for lead are shown graphically in fig. 2, and it will be seen that the relation is practically linear. Extrapolation to the melting-point (327°) gives for γ, 452 dynes/cm.

Fig. 2.



This agrees very well with Hogness, who found 444 dynes/cm. Hogness gives the empirical formula

$$\gamma = 444 - 0·077\,(t - 327)$$

connecting γ and temperature, which gives a decrease of approximately 10·0 per cent. in the value at 980°. The value found in the present work gives a decrease of approximately 8·0 per cent. Hogness's value for tin at the melting-point, 531, also agrees very well with the present value 526. If the decrease in surface tension at 980° is calculated from his formula $\gamma = 531 - 0·080\,(t - 232)$, a value of 12·0 per cent.

approximately is obtained. This is not in agreement with the present work, where a decrease of only 2·5 per cent. has been measured. The above equation was derived from measurements at only three points, 262°, 319°, and 396°, and the last value (396°) was actually higher than the second one.

As pointed out by Hogness, the values for mercury given in the literature vary between 340 and 575 dynes/cm. The figure obtained with the present apparatus for mercury at 19°, 470 dynes/cm., differs only by 1 per cent. from that obtained by Hogness at 20°, 465 dynes/cm.

The values obtained by different observers for tin and lead are given in the following table :—

Observer.	Temp. °	Tin.	Temp. °	Lead.
Quincke *	232	681	327	537 dynes/cm.
Siedentopf *	232	612	327	509 ,,
Grunmach *	232	352	327	482 ,,
Smith	(750–910)	480	(770–780)	424·5 ,,
Hogness	232	531	327	444 ,,
Author	232	526	327	452 ,,

* These values have been taken from the table given by Hogness.

McLeod † has suggested the relation

$$\gamma = C(D-d)^4,$$

where D is the density of the liquid, d that of the vapour, and C is a constant. Ferguson ‡ has put forward

$$\gamma = \gamma_0(1-bt)^n,$$

and states that for non-associated liquids $n=1\cdot21$ gives very good results. In a later paper § he has shown that by eliminating $(1-m)$ between this equation and Kataynia's form of the Ramsay Shields equation, viz.:

$$\gamma\left(\frac{M}{D-d}\right)^{2/3} = A\theta(1-m),$$

McLeod's relation is obtained if $n=1\cdot20$. Sugden ‖ has shown the constancy of $\frac{\gamma^{1/4}}{D}$ for a large number of non-associated liquids up to temperatures approaching the critical temperature, but found that the value of this constant increased slowly with rise of temperature for liquids which are considered to be associated, *e. g.* methyl and ethyl alcohol, acetic acid, amines, etc. The rise in this constant for non-associated liquids up to the boiling-point was usually of the order of 0·5 per cent., while for ethyl alcohol the change was approximately 2·0 per cent. from 20° to the boiling-point, and 5·0 per cent. to 230°. In Table II. the values of $\frac{\gamma^{1/4}}{D}$ are given for mercury (calculated from

---

† Trans. Faraday Soc. xix. p. 38 (1923).

‡ Phil. Mag. (6) xxxi. p. 37 (1916).

§ Trans. Faraday Soc. xix. p. 407 (1924).

‖ Trans. Chem. Soc. cxxv. p. 32 (1924); *ibid.* cxxv. p. 1167 (1924).

Table II.

Mercury.

Temp. °	γ.	D.	$\frac{\gamma^{1/4}}{D}$.
20	465	13·54	·343
22	461	13·54	·342
110	447	13·33	·345
112	454	13·33	·346
155	441	13·22	·346
195	434	13·13	·348
200	436	13·12	·348
251	421	12·99	·349
300	405	12·87	·349
303	408	12·87	·349
354	394	12·76	·349

Tin.

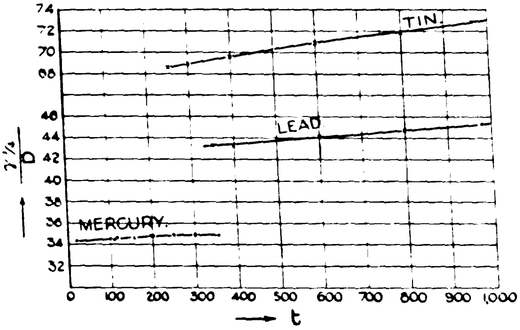
Temp. °	γ.	D.	$\frac{\gamma^{1/4}}{D}$.
253	526	6·982	·686
299	527	6·943	·690
401	526	6·875	·696
600	525	6·755	·709
800	520	6·637	·719
964	514	6·542	·728

Lead.

Temp. °	γ.	D.	$\frac{\gamma^{1/4}}{D}$.
350	453	10·658	·433
400	446	10·597	·4335
600	436	10·359	·441
800	425	10·132	·448
982	414	9·935	·454

Hogness's results) and for tin and lead (*d* has been neglected). They are also shown graphically in fig. 3. It will be seen that the value of this function increases about 2·0 per cent. for mercury and about 5 per cent. for tin and lead. The increase in the value for mercury takes place between 20° and 200°, after which the graph is a straight line. When we consider that a change in this "constant" is found comparable with that obtained for associated liquids over a much greater range of "reduced" temperature, then if the constancy of McLeod's relation is accepted as a criterion of an unassociated liquid, both tin and lead in the liquid state appear to be highly associated.

Fig. 3.



It is proposed to determine the surface tension of a number of other metals and alloys by this method.

Summary.

The surface tensions of liquid tin and liquid lead have been determined between the melting-points and 1000° (approximately).

The values obtained at the lower temperatures agree very well with Hogness's results, but the temperature coefficient of surface tension for tin obtained by him has not been confirmed.

Evidence is brought forward to show that both these metals in the liquid state may be highly associated.

The author would like to thank Dr. W. Rosenhain, F.R.S., for his interest and advice during the progress of this work, and Mr. J. Trotter for assistance in the experimental portion.

XXIX. *Determination of the Modulus of Elasticity by Dynamical Methods.* *By* H. W. Swift, *M.A.*, *B.Sc.*[*]

THE TRUE MODULUS OF ELASTICITY.

IT is well known that the strain or deformation of a material is not in general uniquely determined by the existing system of applied stresses. The elongation of a specimen in simple tension, for example, depends in many cases not only upon the load itself but also upon the method by which this load has been applied, the period over which it has been applied, and the previous elastic history of the specimen.

The deformation which follows a change of static loading may, in the most general case, it appears, be resolved into three separate constituents :—

a. The strain which develops simultaneously with the change in stress, and of which it may be regarded either as the cause or effect. This strain is essentially reversible in nature.

b. A deformation essentially permanent and irreversible which develops more slowly and with the passage of time approaches (in an irregular but roughly logarithmic way) its final value.

c. A strain which develops slowly in a similar way to the permanent set, but which is reversible. This strain is made evident in the partial recovery ("elastic after-strain") which follows the removal of load from so-called semi-elastic materials or from materials which have been overstrained, and in the reversible creep which occurs with elastic materials at high temperatures even under stresses which have apparently no permanent residual effect.

The processes which give rise to these changes are not known, but from the simple fact that strain may have this composite nature it follows that, unless some regard is paid to the factor of time in its definition, the Modulus of Elasticity has no real physical significance and a restricted practical value. Hopkinson[†] has suggested, with reference to metals at high temperatures, that it would be reasonable to define Young's Modulus under such conditions as the ratio of the stress to the instantaneous strain, and this might well be accepted as the general definition of a quantity which would have a clear significance, eliminate (in theory at any rate) the effects of both types of "creep," and simplify the conception of elasticity in overstrained materials.

---

[*] Communicated by the Author.

[†] Proc. Roy. Soc. lxxvi. A, p. 424.

In the case of the elastic materials in common use, below the elastic limit there will as a rule be no creep, so that the effect of time is negligible and values of the modulus obtained at all rates of loading will be practically identical with the true adiabatic elastic modulus. With materials in a plastic or imperfectly elastic state the rate of loading has a considerable effect upon the form of the stress-strain curve, and the strain due to creep is as a rule large compared with the elastic strain. It follows that any tendency to creep is likely, at any normal rate of loading, to have a large effect upon the value of the apparent modulus. Under such conditions values for the "modulus" have no significance unless methods are employed which eliminate the effects of creep entirely. The removal and re-application of a load above the elastic limit give rise to quasi-elastic strains, but it is not possible to say with confidence which portion, if any, of the stress-strain curves so produced corresponds to a truly elastic change, unless the material becomes hardened by prolonged overstrain, in which case there is no assurance that the modulus itself has not undergone modification.

It would appear that where the two types of strain are co-existent no statical method, however rapid the loading, can be relied on to give satisfactory results. There are methods, however, which are able to effect a separation of the two types, and these depend upon the oscillatory movements which take place about the position of equilibrium under small disturbances. The period of such free vibrations is dependent upon the elastic constituent of the strain entirely. The plastic deformation only affects them in so far as it tends to damp them out. It follows that where the period of oscillation can in some simple manner be correlated with the elastic modulus, it affords a very satisfactory method for the determination of this quantity under any condition of stress and strain, and the value so obtained will measure the instantaneous resistance of the material to deformation, and will therefore represent the true elastic modulus.

Dynamical methods of this kind are frequently used to determine the modulus of rigidity, and also to find Young's Modulus for the material of helical springs. To determine the elastic modulus for a straight rod of any section there are two modes of vibration available—longitudinal and transverse.

With most engineering materials the observation of longitudinal vibrations is not easy, the amplitude under ordinary conditions being very small and the periodicity very great. An exception to this is found in the case of wires, where, by the artifice of fixing the wire in span and loading it transversely, the apparent amplitude of vibration can be increased and the periodicity reduced. In this way wires of gauges in common use can, on a convenient scale, be caused to produce elastic oscillations which can be easily observed and timed. Calculation of the modulus is not a difficult matter and the method is found in practice to give very consistent results, even while plastic strain is visibly going on. It has a great additional advantage in that any desired value for the mean tension in the wire may be obtained by adjustment of the load and sag, and the elastic constant so obtained refers to the material in this particular condition.

With sections of greater stiffness this method becomes impracticable, and flexural vibrations are more suited to observation. For practical purposes the most convenient modes of flexural vibration are :

a. Vibrations as a cantilever.
b. Vibrations as a simply supported beam.

It is not possible by these means, nor apparently by other similar methods, to obtain values of the modulus at high stresses, since the period of lateral vibrations becomes less and less dependent upon the elastic properties of the rod as its tension increases. In the outcome this limitation does not appear to be serious, for, with metals at least, it is found from experiments with wire that the true elastic modulus is to all intents and purposes independent of stress or condition of the material over the whole range up to fracture. Hence it would appear that the results obtained by the method of flexural vibrations, at necessarily low stresses, afford elastic data applicable under any conditions. We shall give this method first consideration.

FLEXURAL VIBRATION OF RODS.

Theoretical Basis of the Method.

The conditions which determine the free oscillation of a flexible rod are of course identical with those controlling the rapid vibrations which are commonly associated with the problems of whirling in shafts, and in most cases the same equation of motion can be applied without error. Thus, provided only that external forces, such as gravity, have an effect which is either negligible or constant during oscillation, the fundamental equation is :

$$\mathrm{EI}\frac{\partial^4 y}{\partial x^4}+\frac{w}{g}\cdot\frac{\partial^2 y}{\partial t^2}=0,$$

where w is the weight per unit length of rod.

For a rod of uniform section the general solution of this equation is :

$$y=\cos(pt+\alpha)\,.\,[\mathrm{A}\cos mx+\mathrm{B}\sin mx+\mathrm{C}\cosh mx+\mathrm{D}\sinh mx],$$

in which expression the constants are determined by the length of the rod and conditions of support, and m is related to the period t of a complete vibration :

$$m^4=\frac{4\pi^2}{t^2}\cdot\frac{w}{g\mathrm{EI}}\cdot$$

It follows that if we are able in any instance to evaluate m, and to determine the period t by experiment, then the modulus of elasticity for the material of the rod may be deduced from the relation :

$$\mathrm{E}=\frac{1}{m^4}\cdot\frac{4\pi^2}{t^2}\cdot\frac{w}{g\mathrm{I}},$$

or its "stiffness" from the relation :

$$\mathrm{EI}=\frac{1}{m^4}\cdot\frac{4\pi^2}{t^2}\cdot\frac{w}{g}.$$

It remains to evaluate m for the conditions of support which are likely to be useful in practice.

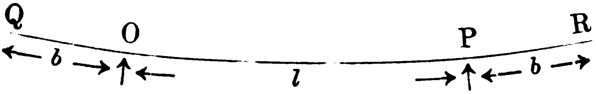
a. *Rod Simply Supported.*

For a rod of any uniform section, oscillating in a principal plane of inertia and simply supported at the ends, the value of m is well known.

For the fundamental vibration $m=\frac{\pi}{l}$.

For a rod under similar conditions, but supported symmetrically at a distance from either end—as may be necessitated in practice by questions of convenience or stiffness—the value of m may be found as follows :

Fig. 1.



Taking origin at O and measuring x in the direction OP, the equations giving the displacement of any point from its position of statical equilibrium are :

for OP, $$\frac{y_1}{\cos(pt+\alpha)} = A_1 \cos mx + B_1 \sin mx + C_1 \cosh mx + D_1 \sinh mx$$

for OQ, $$\frac{y_2}{\cos(pt+\alpha)} = A_2 \cos mx + B_2 \sin mx + C_2 \cosh mx + D_2 \sinh mx.$$

The end conditions are :

$$x=0,\ y_1=0,\quad y_2=0, \qquad x=0,\ \frac{\partial y_1}{\partial x} = \frac{\partial y_2}{\partial x},$$

$$x=l,\ y_1=0,\quad x=-b,\ \frac{\partial^2 y_2}{\partial x^2} = \frac{\partial^3 y_2}{\partial x^3} = 0, \qquad \frac{\partial^2 y_1}{\partial x^2} = \frac{\partial^2 y_2}{\partial x^2},$$

$$x=\frac{l}{2},\ \frac{\partial y_1}{\partial x} = 0.$$

From these eight conditions it is possible to eliminate the seven ratios between the constants $A_1 A_2 B_1 B_2 C_1 C_2 D_1 D_2$ and to deduce the relation :

$$\tanh\frac{ml}{2} + \tan\frac{ml}{2} = 2 \cdot \frac{1 + \sec mb \operatorname{sech} mb}{\tan mb - \tanh mb},$$

which determines the value of m.

In order to obtain this expression in a form suitable for practical application, let the right-hand side be expanded in terms of mb. The result up to and including terms of the sixth order in $\frac{1}{mb}$ is

$$\tanh\frac{ml}{2} + \tan\frac{ml}{2} = \frac{6}{m^3 b^3},$$

and it can be shown that for small values of the ratio $\frac{b}{l}$ a close approximation to the exact solution is given by

$$\frac{ml}{2} = \frac{\pi}{2} - \frac{m^3 b^3}{6}.$$

Hence $$\frac{ml}{2}=\frac{\pi}{2}\left\{1-\frac{\pi^2b^3}{3l^3}\right\}\text{ nearly,}$$

and the value of the modulus for short overhangs is

$$\mathrm{E}=\frac{4}{\pi^2}\cdot\frac{wl}{g\mathrm{I}t^2}\left(l^3+\tfrac{40}{3}b^3\right).$$

Experimental tests show that this relation holds well for values of the ratio $\frac{b}{l}$ up to 0·2, the correction in that case being over 10 per cent.

For values of the overhang not exceeding $\frac{1}{12}$ span the correction is less than 1 per cent. and may usually be neglected.

b. *Rod as Cantilever.*

For a fairly stiff rod of uniform section fixed as a horizontal cantilever the value of m is well known:

$$m=\frac{1{\cdot}875}{l}.$$

When the length l is measured along the rod, this value is found to give good results when the deflexion at the end does not exceed about $l/6$. For more flexible sections the rod is more conveniently fixed as a vertical cantilever, but the value of m will in that case be influenced by the fact that gravity will increase (if the rod hangs downwards) or decrease (if it stands erect) the elastic restoring force, and will therefore have an effect upon the periodicity.

The equation of motion in this case contains an additional term due to the effect of gravity, and for a rod hanging vertically downwards takes the form:

$$\mathrm{EI}\frac{\partial^4 y}{\partial x^4}+w\frac{\partial y}{\partial x}+\frac{w}{g}\frac{\partial^2 y}{\partial t^2}=0,$$

where w is the weight per unit length of rod.

If we assume as a solution:

$$y=u\sin(pt+\alpha),$$

where $\begin{cases} u \text{ is a function of } x \text{ independent of } t, \\ p,\ \alpha \text{ are independent of } x, \end{cases}$

then u must satisfy the equation:

$$\frac{\partial^4 u}{\partial x^4}+\frac{w}{\mathrm{EI}}\frac{\partial u}{\partial x}-\frac{p^2w}{g\mathrm{EI}}u=0.$$

If the effect of gravity is negligible the centre term disappears. In a large range of useful cases its value will be small. Under these circumstances it is justifiable to apply an approximate method for the solution of the equation :

$$D^4 + \frac{w}{EI} D - \frac{p^2 w}{gEI} = 0,$$

or

$$D^4 + \alpha D - \beta^4 = 0, \text{ say.}$$

Writing $D = \beta + \epsilon$ where ϵ is small, we find

$$\epsilon = -\frac{\alpha}{4\beta^2} \text{ nearly.}$$

Hence

$$D = \beta - \frac{\alpha}{4\beta^2},$$

and the complete approximate solution may be written :

$$u = (A \sin \beta x + B \cos \beta x)(1 + \gamma x) + (C \sinh \beta x + D \cosh \beta x)(1 - \gamma x),$$

where

$$\gamma = \frac{1}{4p}\sqrt{\frac{wg}{EI}}.$$

The end conditions are :

$$x = 0, \qquad u = 0, \qquad \frac{\partial u}{\partial x} = 0,$$

$$x = l, \qquad \frac{\partial^2 u}{\partial x^2} = 0, \qquad \frac{\partial^3 u}{\partial x^2} = 0.$$

By applying these conditions and eliminating ABCD, an equation results which may be reduced to the form :

$$1 + \cos \beta l \cosh \beta l = \frac{2\gamma}{\beta}(\cos \beta l \sinh \beta l - \sin \beta l \cosh \beta l),$$

where $\frac{\gamma}{\beta}$ is small.

The approximate solution of this equation is

$$\beta l = \beta_0 l + \frac{2\gamma}{\beta},$$

where $\beta_0 l$ is the value (1·875) of βl when $\gamma = 0$.

Hence the angular velocity p corresponding to the vibratory motion is given by

$$\left[\frac{p^2 w}{gEI}\right]^{\frac{1}{4}} l = \beta_0 l + \left[\frac{g^3 w}{p^6 EI}\right]^{\frac{1}{4}},$$

and knowing the period $t=\frac{2\pi}{p}$ the modulus of elasticity can be found by the formula :

$$E=\frac{4\pi^2 l^4 w}{\beta_0{}^4 g I t^2}\left(1-\frac{2gt^2}{4\pi^2 l}\right)$$

$$=3\cdot 20\frac{wl^4}{gIt^2}\left(1-\cdot 051\frac{gt^2}{l}\right) \text{ nearly.}$$

If the rod be fixed as a cantilever standing erect, the signs of α, γ in the above analysis will be reversed, and we have finally :

$$E=3\cdot 20\frac{wl^4}{gIt^2}\left(1+\cdot 051\frac{gt^2}{l}\right) \text{ nearly.}$$

c. *Rod Simply Supported and Loaded at Centre.*

The vibration of a uniform rod with a single concentrated load is treated exactly by Dunkerley *, who obtains an implicit equation in m. If the concentrated load is central it is possible to reduce this equation to the form :

$$\frac{\left\{1-\frac{\alpha}{4}(\tan\theta-\tanh\theta)\right\}\left\{1+\frac{\beta}{4}\,\frac{\tan\theta-\tanh\theta}{\tan\theta\tanh\theta}\right\}}{\tan\theta-\tanh\theta}=0,$$

where $\alpha=\frac{Ww^2}{m^3 gEI}$, $\beta=\frac{w^2 I'}{mEI}$, $\theta=\frac{ml}{2}$.

The solution to the present problem is

$$\tan\theta-\tanh\theta=\frac{4}{\alpha}=\frac{4w}{Wm},$$

and the value θ of $\frac{ml}{2}$ for any value of the ratio $\frac{W}{wl}$ is given by the equation :

$$\theta(\tan\theta-\tanh\theta)=\frac{2wl}{W}. \quad \ldots\ldots \quad \text{(i.)}$$

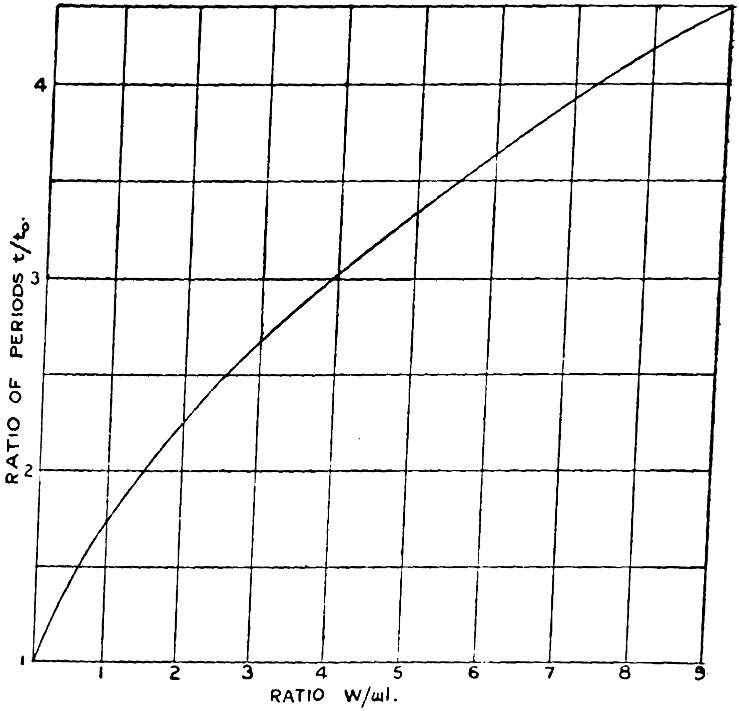
For assumed values of θ a curve can be plotted (fig. 2) and the relation between $\frac{wl}{W}$ and $m=\frac{2\theta}{l}$ can be established to any required degree of accuracy.

It is of interest to note that $\theta=\frac{\pi}{4}$ when $\frac{W}{wl}$ is approximately 7, showing that by loading a rod centrally to this extent the period of vibration will be quadrupled.

---

[*] Dunkerley, Phil. Trans. Roy. Soc. vol. clxxxv.

Fig. 2.—Effect of Central Loading on Periodicity of simply supported Beam.



TECHNIQUE OF THE METHOD.

(a) *Accuracy.*

The form of the expressions obtained for the modulus makes it clear that some of the measurements require more careful determination than do others. For example, in each case the modulus varies inversely with the square of the period of oscillation, so that errors in timing will be doubled. Where no artificial device is available for the counting of vibrations, accurate results cannot ordinarily be expected if the period is much less than 0·3 second. This limits to some extent the convenient application of the method and is discussed in more detail later. From the present experimental work it appears that with this reservation a reliable value for the periodicity can be expected if two tests are made, each over not less than a hundred oscillations and of not less than one minute's duration.

In determinations by the lateral vibrations of rods errors in the applied value of $ml=\theta$ will be quadrupled, and it follows that this must be known with more than usual accuracy. Approximate relations which are admirably suited to the estimation of whirling speeds require examination before they can be accepted for the determination of the modulus of elasticity, and for that reason approximate methods have where possible been avoided in the theoretical treatment and where unavoidable have been checked experimentally.

Careful measurement of the cross-section and length of the bar will also be necessary. For similar accuracy greater care is required in the computation of the sectional moment of inertia than merely of the sectional area. If the stiffness EI is required, of course, no measurement of the cross-section is necessary. There is no difficulty in measuring the length with sufficient accuracy when the rod is simply supported, but in other cases it is important that the end which is encastré should be very securely fastened in a massive clamp. Otherwise insensible movement in the clamp may increase the effective length of the rod and seriously prejudice the results. In the present experiments the bars used were clamped horizontally in a 25 ton testing machine over 18 inches of their length, and in the case of a round bar one inch in diameter it was found that a measurable error was introduced if the distributed pressure fell to 5 tons.

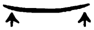
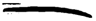
(b) *Experimental Results.*

Experiments were made in the first place to test the accuracy of the methods proposed and to verify the results obtained.

a. In Table I. are shown values of the modulus obtained by the method of flexural vibrations compared with determinations made by extensometer on a short length of the same rod, and also by measurement of the deflexion of the rod as a simply supported beam with central load. The agreement in most cases is considered good. The heavier bars show a tendency to give low results when fixed as vertical cantilevers, but this is almost certainly due to imperfect rigidity in the clamps employed, the importance of which has been mentioned. No present explanation is offered for the low figure obtained from bending of the flat section. The tests, however, seem to afford satisfactory evidence that the method is practicable and capable of good accuracy, and indicate that it may generally be applied with less trouble and more confidence to stiff rods when simply supported. With lighter and more flexible rods, however, it is found that oscillations are more readily made to persist under encastré conditions, and in these cases secure clamping presents no difficulty.

Table I.

Comparative Values of Young's Modulus obtained by Statical and Dynamical Methods.

Rod.	Values of Young's Modulus.				
	Extensometer.	Oscillations. 		Vertical.	Bending.
Steel:					
¾ in. round......	29·7	30·2	29·9	29·8	29·9
1 in. round......	29·5	29·7	29·4	(28·6)	29·6
1 in.×½ in. flat.	28·9	29·0	28·5	28·5	(27·8)
$\frac{3}{16}$ in. round ...	29·5	—	29·4	—	29·0
Copper:					
⅝ in. round	17·9	18·2	18·0	17·9	17·9
Same Annealed...	17·5 18·3	18·1	17·9	17·6	—

b. Table II. gives the results of the tests made to verify the correction proposed for the overhang of simply supported rods. It will be seen that the results are reasonably consistent, and there is no serious deviation up to an overhang at each end of a fifth of the span.

Table II.

Test of Correction for Overhang.

¾ in. round, Steel.		
Ratio of Overhang. *b/l*.	Young's Modulus. E.	Correction Applied. per cent.
·005	30·3	nil
·065	30·2	0·4
·10	30·1	1·3
·14	30·1	3·7
·18	30·0	7·7
·21	29·8	12·5

c. Experiments were made to confirm the relation between $ml=\theta$ and $\frac{wl}{W}$. In these tests a steel rod and also a copper tube were used, and out of 25 determinations of θ none differed by more than $\frac{1}{2}$ per cent from the theoretical value derived from equation (i.). The greatest load was sixteen times the weight of the rod.

d. Table III. gives values of the product EI for sections of a form inconvenient for extensometer tests. These are derived from oscillations and from careful measurements of static deflexion under load. The bar was in each case simply supported (on light rollers) and in some cases was subjected to a central load.

TABLE III.

Determination of Stiffness EI by Oscillations.

Section.	Value of EI.	
	Bending.	Vibration.
Steel: 1 in. angle...	419×10^3	421×10^3
$2\frac{1}{2}$ in. angle..	$10{\cdot}5\times10^6$	$10{\cdot}6\times10^6$
Copper: $\frac{5}{8}$ in. tube..	315×10^2	310×10^2

e. As a test of the validity of the method in the case of imperfectly elastic materials, the copper rod already used was annealed along its entire length and then subjected to tests by vibrations and by extensometer. The bending test was impracticable as the bar sagged continually under its own weight. In spite of this oscillations persisted sufficiently to give the results shown in Table I. These seem to afford definite proof that the method does effectively separate the elastic extension from plastic creep and also suggest that the true elastic modulus is not appreciably modified by annealing. The slight difference recorded may be due to incorrect measurement of the section, which showed slight irregularities owing to scaling during the process of annealing. The stress-strain relation revealed by the extensometer was nowhere linear, and the figures given in the table are derived from the earlier part of tests during which the load was being removed from the specimen after several applications.

(c) *Applications.*

The method of flexural vibrations is put forward primarily for its scientific value as one capable of separating the truly elastic from other forms of strain and of determining the true elastic modulus. For this purpose it appears to be admirably suited. The apparatus required is of the simplest type, no manipulative skill is necessary, and the results are reliable and accurate.

It is not suggested that the method is able in any general way to take the place of the usual extensometer test where information is sought regarding the static stress-strain relations of a material. Any dynamical method is by nature unsuited for such a purpose. But there are certain practical cases of materials which are perfectly elastic, or materials which by mechanical treatment will become perfectly elastic before employment, in dealing with which the method of oscillations has distinct possibilities. In the first place a whole rod or bar of the material may be used for the test, so that no cutting or preparation of a specimen is necessary whatever shape the section may be, a considerable saving in the case of sections whose shape renders them inconvenient to test by extensometer. Furthermore, where a section is to be employed as a beam or strut, the quantity upon which the design is based is the product EI of the elastic modulus and sectional moment of inertia. It is this product which also determines the period of flexural vibrations, so that without any measurement of the cross-section it is possible to calculate the stiffness of the rod from a knowledge simply of its length, period of oscillation, and conditions of support. With the lighter forms of rolled and extruded sections, the sectional moment of inertia requires very careful measurement, and in such cases the method may actually give more ready and reliable information of the behaviour of the section as a beam or strut than separate determination of the moment of inertia and modulus of elasticity, which the use of an extensometer would necessitate.

The range of sections over which the method may conveniently be employed is limited by the accuracy with which the timing can be carried out. It has been pointed out that the shortest period which is likely to afford reliable results is about 0·3 second. Table IV. has been drawn up on this basis and shows the least length of a number of sections upon which tests of this kind may be satisfactorily made when the section is unloaded and simply supported at the ends. Where bars of the necessary length are available, experiment has shown that this method of support is as a rule the most suitable. When very light rods (the 3/16 diameter tie rod referred to in Table I. is a case in point) are tested in this way, it may be found that owing to flexibility the oscillations damp out rapidly. In such cases it will be more convenient to fix the rod as a cantilever, a process which will be found to give persistency to the vibrations and will also increase their period. A similar effect to a lesser degree is obtained if the rod is made to overhang at each end of the simply supported span.

TABLE IV.

Young's Modulus by Oscillations, Unloaded in Span. Minimum Lengths Suitable.

Section (Steel).		Minimum length.
Joists:		feet
BSB 1	$3 \times 1\frac{1}{2}$	15
2	3×3	22
8	6×3	20
12	8×4	23
17	10×5	27
Channels:		
BSC 1	$3 \times 1\frac{1}{2}$	17
7	6×3	24
20	$10 \times 3\frac{1}{2}$	26
Angles:		
BSEA 5	$2 \times 2 \times \frac{3}{8}$	16
9	$3 \times 3 \times \frac{3}{8}$	20
14	$6 \times 6 \times \frac{5}{8}$	28
Tees:		
BST 6	$2 \times 2 \times \frac{5}{16}$	17
15	$4 \times 4 \times \frac{3}{8}$	23

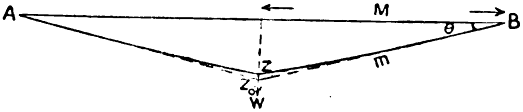
When bars are employed whose section is too stiff or whose length is too short for this method, the period of vibration may be increased by the addition of dead weights at the centre. The extent to which this device will affect the period is indicated by fig. 2, which is derived from equation (i.).

The $2\frac{1}{2}$-inch angle referred to in Table III. would have given a period of 0·123 second unloaded. By applying a central load of 306 pounds the period was increased to 0·36 second, which is readily measurable. The extent to which this artifice can be applied is determined by the beam strength of the bar. It will be noted in this connexion, that since the period is for large central loads nearly proportional to $W^{\frac{1}{2}}l^{\frac{3}{2}}$, whereas the maximum stress in the beam is proportional to Wl, the period for a given maximum stress will vary directly with the length l. Hence the greater the length of the bar available, the more probable is it that the vibrations can be made sufficiently slow for measurement without overstressing the material.

OSCILLATIONS OF A WIRE IN SPAN WITH CENTRAL LOAD.

Consider a flexible wire of weight wl supported across a span 2M loaded centrally as shown in the figure.

Fig. 3.



The oscillations under consideration are those which would follow the sudden release of a small additional load at the centre.

At any instant we shall suppose the tension at the ends of the wire to be T, acting at an angle of θ with the horizontal, and that the central sag is Z.

Writing
$$\begin{cases} Z_0 = M\tan\theta, \\ m = \text{chord AZ}, \end{cases}$$

we have
$$\begin{cases} \delta\theta = \dfrac{\cos^2\theta}{M}\delta Z_0, \\[2ex] \dfrac{\delta T}{aE} = \dfrac{\delta m}{m} = \tan\theta \, . \, \delta\theta, \end{cases}$$

where E is the *apparent* modulus of the wire in span.

The upward force P tending in any position to restore equilibrium is

$$P = 2T\sin\theta - (W + wl).$$

Hence
$$\begin{aligned} \delta P &= 2\sin\theta\,\delta T + 2T\cos\theta\,\delta\theta, \\ &= \frac{2EaZ_0^2\cos^3\theta}{M^3}\delta Z_0 + \frac{2T\cos^3\theta}{M}\delta Z_0. \end{aligned}$$

This will give rise to simple harmonic oscillations of period t given by

$$\frac{2Ea}{M^3}Z_0^2\cos^3\theta + \frac{2T}{M}\cos^3\theta = \left(W + \frac{wl}{2}\right)\frac{4\pi^2}{t^2 g},$$

where $T = \dfrac{W + wl}{2\sin\theta}$.

The apparent modulus may therefore be derived from experimental figures by the relation :

$$aE = \frac{W + \frac{wl}{2}}{t^2 Z_0^2 \cos^3\theta} \cdot \frac{2\pi^2 M^3}{g} - \frac{M^3(W + wl)}{2Z_0^3 \cos\theta},$$

and since $$\frac{Z_0}{Z} = \frac{M}{m} \cdot \frac{W + wl}{W + \frac{wl}{2}},$$

it follows that

$$aE = \frac{2\pi^2 M^3}{g} \cdot \frac{W + \frac{wl}{2}}{t^2 Z^2}\left(1 - \frac{gt^2 \cos\theta}{4\pi^2 Z}\right)\left[\frac{W}{W + wl} \cdot \sec^5\theta\right],$$

where $\sec^5\theta = 1 + \frac{5}{2} \cdot \frac{Z^2}{M^2}$ under normal conditions.

In this expression the terms in the square bracket may be regarded as corrective upon the remainder, and in a particular determination either or both may be negligible according to the conditions. It is possible where great accuracy is required that certain other corrections must be applied for curvature in span and for stiffness in the wire, but under practical conditions it will usually be found that the tension necessary to eliminate kinks and coiling in the wire will be sufficient also to render these corrections unnecessary.

It can be shown that the fractional correction for curvature in span is

$$+\frac{w^2 m^2 aE}{12T^3}.$$

For a steel wire 0·1 inch in diameter across a total span of 50 feet, this correction is about 1 per cent. under a tension of 80 pounds.

The correction for stiffness will depend upon the means of support at the ends.

If a wire is held in flexible clips the fractional correction is $-2\sqrt{\frac{EI}{Tm^2}}$, and for the same steel wire is below 1 per cent. for tensions above 60 pounds. In the case of a wire clamped horizontally at the ends this correction is doubled.

Experimental Verification.

a. In order to check the truth of these results and the accuracy of the method, experiments were made with steel piano wires whose elastic range was known to be large.

The wire under test was fixed across a span of about 35 feet, each end being held in a light clamp carried on a small radial ball-bearing to ensure flexibility. The spindles carrying the bearings were bolted firmly to the under side of a stiff girder. The central dip of the wire under test was measured on a steel scale which was suspended from the girder close to the wire and calibrated by means of a dumpy level. The tension in the wire was controlled by variations in the sag and load.

Determinations were made covering a range of tensile stress up to 80 tons per square inch with various values of the dip, and the results showed that provided the tension was above a certain minimum (about 40 pounds) the value of the modulus deduced was consistent and agreed well with the values obtained by statical methods. Over a hundred determinations were made, and with two or three exceptions all were within 1 per cent. of the mean values.

It was concluded from these tests that the method was free from systematic errors and capable of good accuracy.

b. The ability of the method to separate elastic from other types of strain was tested and confirmed by the use of a soft copper wire.

In spite of a final elongation of about 35 per cent. and in spite of the continuance of a visible creep during many of the periods of test, the value of the modulus (calculated on the sectional area at the time of test) was found to correspond with that obtained by statical methods during unloading (after prolonged straining), and to be constant for all values of the tension up to the point of fracture. It should be pointed out that in some instances immediately following an addition of load the creep was so rapid that oscillations were damped out before a determination of periodicity could be made, but there was in no case any evidence of variation in the period.

It seemed reasonable to conclude from these experiments that the method does effectively eliminate all but elastic strains, and gives a consistent value for the true elastic modulus.

c. The method was now applied to investigate the elastic properties of certain other wires, soft iron, hard drawn brass, and duralumin being employed.

The values of the modulus obtained over the elastic range agreed well with the results of statical methods and are shown in Table V. In order to determine the effect of plastic strain and high stresses upon the elastic properties of the wires, the experiments were continued at tensions above the elastic limit. The damping effect of creep was sometimes evident with the iron wire, and in order to reduce the sag to convenient values it was necessary to shorten the wires after permanent set had begun to develop. Calculations were based in each case upon the sectional area at the time of test. The results showed that the value of the modulus is substantially the same at all tensions up to the point of fracture with each of the wires employed. A progressive diminution amounting finally to 3 per cent. was recorded in the case of the brass wire at high tensions, but no systematic change whatever could be detected in the soft iron or duralumin wires.

TABLE V.

Modulus for Wires by Oscillations.

Wire.	Value of E.	
	Statical.	Oscillation.
Piano	28·5	28·7
„ (annealed)	28·4	28·8
Iron	27·3	27·4
Brass	14·9	14·9'
Duralumin	10·25	10·3
Copper (annealed)	15·7	15·85

The experiments described above were carried out at the University of Leeds.

CONCLUSIONS.

The results of the experiments with copper, iron, duralumin, and brass wire give definite support to the opinion that truly elastic strain is quite independent of any other form in development as well as origin, and show that it is possible to effect with certainty a separation in stress-strain relations between the elastic and non-elastic components of strain. They suggest moreover that elasticity is a definite inherent property of materials which is not destroyed by mechanical treatment and overstrain, and that its modulus remains practically unaffected by the elastic history and condition of the specimen. It will be interesting to trace the effects on this constant of heat treatment and temperature.

XXX. *The Variation of Pressure with Temperature in Evacuated Vessels. By* N. R. Campbell. (Communication from the Staff of the Research Laboratories of the General Electric Co., Wembley *.)

Summary.

If a well baked and exhausted glass vessel is carried through a cycle of heating to a temperature T_a and cooling to a temperature T_b, a condition is reached rapidly in which the pressures p_a, p_b, at these temperatures are repeated. If T_a is varied while T_b is fixed, both p_a and p_b are functions of T_a which depend also in a complicated manner on the constitution and preparation of the vessel.

If to this cycle is now added a stage in which the gas is "cleaned up" by the discharge, both p_a and p_b decrease with repetition of the cycle, until final values are reached which are again both functions of T_a, but now depend much less on the constitution and preparation of the vessel. If $T_a = 120°$ C., $T_b = 20°$ C., p_b is of the order of 10^{-5} mm.

If the walls of the vessel are coated with a layer of metal (Ni, Mo, W) the statement of the first paragraph remains true; but, while the clean-up still produces a temporary reduction of pressure, it does not produce the progressive permanent change described in the second paragraph. If, in place of these metals, Mg, Zu, Cu, Ag are used, subsidiary complications enter that are discussed in the test.

Attempts to determine by various methods the nature of the residual gas involved in these changes were not very successful, but indicate (in accordance with expectation) that H_2O and CO_2 are the main constituents.

The facts relating to the metal-coated vessels seem in accordance with existing ideas, but throw no light on the still doubtful question what is the means by which the discharge promotes adsorption of gas. The more complicated facts relating to the bare glass vessels require more explanation. A very tentative theory is suggested, according to which the discharge in such vessels, besides promoting adsorption, induces a chemical reaction involving the glass which leads to the permanent removal of some of the gas; at the same time the glass is capable of disolving the gas with the formation of saturated solutions which have at the temperature T_a the vapour-pressure p_a; gas is continually introduced into the vessel from the outside by diffusion of these solutions through the glass, and prevents p_a from falling below this value in virtue of the removal of gas by the chemical reaction.

---

* Communicated by the Director.

Some practical conclusions arising from the facts described are mentioned. Permanent low pressures ($<10^{-6}$ mm.) in sealed-off vessels appear to be obtainable only if the glass walls are coated with metal. A reason is given why gas adsorbed on a metal surface cannot be removed by prolonged baking of the glass vessel in which it is contained, although it can be removed with great ease and rapidity by heating the metal in the cool glass vessel.

(1) *Outline of the Observations.*

IF a glass vessel is baked at a temperature T during exhaustion to a low pressure p, sealed off and heated to a temperature T′ less than T, the pressure will rise and approach asymptotically a pressure p' greater than p. This fact appears to have been established first by Shrader [*]; some additional facts were recorded in a previous paper from these laboratories [†]. We now propose to describe a more detailed study of the changes of pressure associated with changes of temperature in well-baked and well-exhausted vessels.

The vessels were constructed as ionization gauges. The walls were composed of four different glasses, A, B, C, D; the cathode was always a tungsten filament; the grid and anode were usually of nickel, but sometimes of molybdenum or tungsten. These changes in the materials of the vessel, which were accompanied by changes of geometrical form, had no ascertainable effect on the results, and accordingly it is not necessary to describe them in detail; but particulars of the four glasses are given in an appendix.

After the vessels had been well exhausted at a temperature not less than 380° C., they were subjected to three operations:—(*a*) heating to a temperature T_a which lay between 50° and 200° C.; (*b*) cooling to "room temperature" T_b between 13° and 20° C.; (*c*) "cleaning-up" or reduction of pressure to p_c by the passage of a suitable discharge from the thermionic cathode.

Since in (*a*) and (*b*) the pressure approaches a final value asymptotically, a slow change being still perceptible after 24 hours, it was necessary practically to fix conventionally the period of each of these operations. The periods ranged from 20 to 44 hours; the effects of variation within this range were masked by other irregularities. Again no significance must be attributed to the exact values of p_c; they depend on the period and conditions of the clean-up. So long as p_c is considerably lower than the preceding p_b, its precise value is of no importance.

---

[*] J. E. Shrader, Phys. Rev. xiii. p. 434 (1919).

[†] Research Laboratories of the G. E. C., Phil. Mag. xlviii. p. 553 (1924).

A typical series of observations is detailed in Table I.; the numerals in the first column serve to identify the operations and denote their order.

TABLE I.

Pressures in 10^{-6} mm. calculated from the reading of an ionization gauge, assuming that the gas is nitrogen.

	p_a.		p_b.	p_c.
	(T_a=200° C.)	(T_a=120° C.)	(T_b=13°-20° C.)	
1	—	—	13·4	—
2	—	—	—	0·6
3	—	183	—	—
4	—	—	130	—
5	—	—	—	1·3
6	—	98	—	—
7	—	—	57	—
8	—	—	—	0·8
9	—	50	—	—
10	—	—	27	—
11	—	—	—	0·1
12	—	28	—	—
13	—	—	13·6	—
14	—	—	—	0·1
15	—	35	—	—
16	—	—	13·9	—
17	—	—	—	2·1
18	—	24	—	—
19	—	—	12·8	—
20	450	—	—	—
21	—	—	290	—
22	—	—	—	1·1
23	290	—	—	—
24	—	—	140	—
25	—	—	—	0·8
26	190	—	—	—
27	—	—	100	—
28	—	—	—	1·2
29	150	—	—	—
30	—	—	80	—
31	120	—	—	1·2
32	—	—	80	—
33	—	—	—	0·8
34	130	—	—	—
35	—	—	75	—

Considering first 1 to 4, we see that the first heating produces an increase of pressure which is not reversed by cooling. (This increase would have been the same if the clean-up at 2 had been omitted.) But if, after 4, operations *a* and *b* had been repeated alternately without *c*, no further progressive change would have occurred; p_a and p_b would have repeated themselves, and, apart from minor irregularities (which may have been due in part to lack of control of the temperatures), the pressure would have appeared a definite function of the temperature. But when a clean-up is interpolated, as at 5, a permanent change is produced; at 6 and 7 the pressure would again be found to be a definite function of the temperature if *a* and *b* were repeated, but the values would both be lower than before the clean-up at 5. Repetition of *a*, *b*, *c* in cylindrical order reduces these pressures further until, from 7 to 19, the pressures at the high and the low temperatures reach final values which are unaltered even if the vessel is cleaned up.

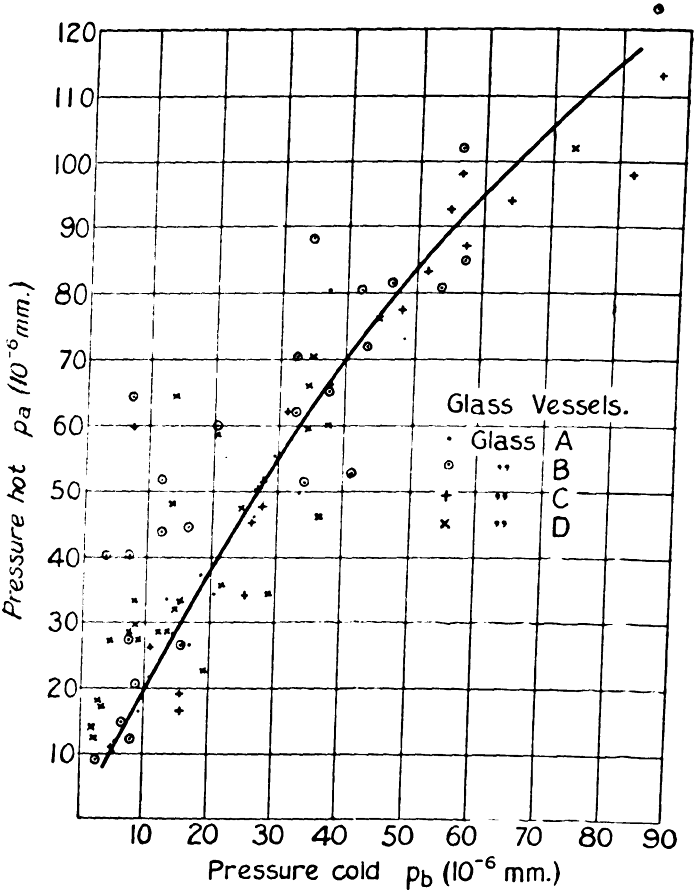
When the temperature in *a* is raised, as at 20, the whole cycle of changes is repeated. There is first an increase of the equilibrium pressure at room temperature. If the vessel is heated and cooled, without intermediate clean-up, the pressure corresponding to each temperature is fixed; but the clean-up reduces these pressures gradually until a final state is reached in which the relation between pressure and temperature is unchanged by the clean-up. It is to be noted that the final pressure at T_b after heating to 200° is markedly greater than the final pressure at the same temperature after heating to 120°; the pressure is a definite function of the temperature only so long as the cycle of heating and cooling remains unchanged. In order to recover the lower value after *b* (*e.g.* that at 19), it would be necessary to repeat the cycle *a*, *b*, *c* several times, with the lower value of T_a.

(2) *The Pressure-Temperature Coefficient. Glass Vessels.*

Observations similar to those of Table I. were made on a large number of vessels, and attempts were made to co-ordinate the absolute values of the pressures. One regularity that could be detected is shown in fig. 1. Here p_a is plotted against p_b; in each case T_a was about 120°, and p_a is compared with the p_b immediately following.

The deviations of most of the points from the line drawn through them do not exceed markedly the irregular variations shown in Table I. between the values obtained on repetition of a cycle in which there is no progressive change. There is, however, a group of points which diverge markedly, all lying well above the line in the region of small pressures. It is probable that for these points p_b is misleadingly small. For in all cases the reading of the ionization gauge involves a change of pressure; there is usually a slight rise of pressure, due to the heating of the electrodes, followed by a fall, due to the clean-up. The pressure recorded is always the first that can be read, and normally does not differ markedly from the maximum; but in the discrepant vessels the initial rise is abnormally large;

Fig. 1.



if the maximum had been recorded in all cases, the discrepancy would have disappeared. If it is neglected for the moment (for there are also normal points in the same region of pressure), the experiments shown in the figure indicate that there is a relation between p_a and p_b, which may be roughly described as defining a temperature-coefficient of the pressure, independent of (1) the nature of the glass and of the electrodes within the limits investigated, and (2) of whether the pressures have or have not been reduced by the clean-up. It is not certain that the relation is not also independent of T_a; for observations in which this temperature was 200° C. seem to be also near the curve; but the number of these observations was so small that it would be unwise to base much on them. Here it may be pointed out that the experiments are tedious and that each point implies a lapse of at least two days; the experiments of Table I. occupied five weeks.

Many attempts were made to discover a relation between the treatment of the vessel on the pump and the value of p_b after the first heating, but no success was obtained. Very high values of p_b can be avoided by prolonging the period of baking and pumping, but there was no evidence that the continuance of these processes for more than a few hours had any effect. A vessel which had been baked on the pump for 24 days at temperatures gradually reduced from 400° C. to 250° C. differed in no way from others sealed off after two hours' baking at 360°.

On the other hand, the important fact appeared that the final values of p_a and p_b were never very different, whatever were the initial values. The initial p_a (*i. e.* the value after the first heating to 120° C.) varied in these experiments between 40 and $1{\cdot}5\times10^{-4}$ mm.; the final value attained after many repetitions of the cycle *a*, *b*, *c* varied between $0{\cdot}14$ and $0{\cdot}06\times10^{-4}$ (in normal vessels), and there was no correlation between the initial and final values. It appears that by the repetition of that cycle vessels of this type can be reduced to a definite state which is always very nearly the same and is independent within wide limits of their previous history.

(3) *Metal-coated Vessels.*

In the exhaustion of these vessels discussed so far, the electrodes were heated in the usual way to drive off gas, but care was taken not to raise the temperature so high that there was any appreciable evaporation of the metal and blackening of the walls. In another series of experiments the walls were deliberately blackened with evaporated nickel.

It is well known [*] that the pressure in a vessel can be greatly reduced by this process; though it was originally described in connexion with the evaporation of tungsten, the reduction is not confined to this metal. Accordingly, if all gas had been carefully removed from the metal before evaporation and the vessel was sealed off immediately afterwards, the resulting pressure was very much lower than any that could be obtained by mere pumping. But if it had not been removed completely, so that the gas was evolved from the heated metal during evaporation, the pressure was not less, but usually greater, than that in the vessels with unblackened walls.

With vessels prepared in this manner, the results were definitely changed. In the first place the clean-up produced no progressive change in p_a and p_b; the vessel could still, of course, be cleaned up by the discharge to a pressure less than p_b, but, however often the clean-up was repeated, the values of p_a, p_b obtained after the first cycle of heating and cooling remained unchanged.

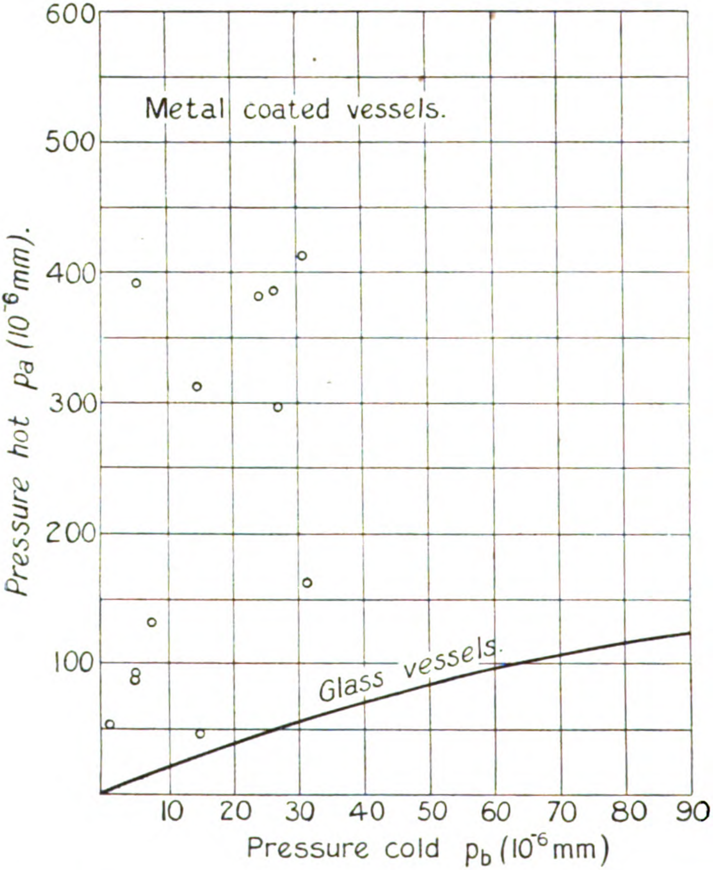
In the second place the ratio of p_a to p_b, represented in fig. 2, was considerably higher. The line in this figure refers to glass vessels and is transferred from fig. 1; the points refer to vessels of which the walls were coated with metal; it is clear that they define a temperature-coefficient much higher than that of the unblackened vessels. The points for these vessels are necessarily fewer, because now each vessel will give only one point; several points cannot be obtained for the same vessel by means of the clean-up. Further, the vessels shown are those in which p_a and p_b were relatively high because gas was evolved during the deposition of the metal. Those in which this evolution was avoided, and consequently the pressure was very low, cannot be shown on the same scale. The measurements at these very low pressures are somewhat inaccurate, but there was no doubt that the very highly evacuated vessels showed also the increased temperature-coefficient of the pressure. It is difficult to prepare vessels in which the pressure after sealing off and heating will have a prescribed value.

Exactly similar results were obtained when the walls were blackened with tungsten or molybdenum by exploding wires, or again when nickel was deposited from the carbonyl by warming the walls, instead of by evaporating the anode. In none of the matters discussed here could any difference between these three metals be detected. Attempts to use silver, copper, magnesium, or zinc failed. When silver or copper was deposited on the walls, either by evaporation or by chemical deposition, there was no equilibrium pressure at 120° or high temperatures; the pressure increased steadily as long as the heating was continued. At the same time, the deposit changed in appearance and ultimately became transparent. It is clear that, even at this comparatively low temperature, there is some reaction between the metal and the glass which introduces a new and disturbing factor. With magnesium

---

[*] *Cf.* S. Dushman, 'High Vacua,' p. 172.

Fig. 2.



or zinc again it was impossible to measure the pressure satisfactorily on the ionization gauge; for the clean-up was so rapid that the pressure changed materially during the few seconds required to take an observation. The clean-up proceeds, though more slowly, even when no anode voltage is applied; the mere presence of the hot filament seems to cause the disappearance of the gas in the presence of these metals, just as it does in their absence when the gas is hydrogen. But such measurements as could be made indicated again a temperature-coefficient of the metal-coated vessels greater than that for those with bare glass walls.

This difference is important in the interpretation of the results, for it leads at once to the rejection of the most obvious explanation of the progressive action of the clean-up to the glass vessels. At first this was naturally attributed to the gradual formation of a film of sputtered or evaporated metal on the walls; for such a film will produce all the effects of a metal-coated surface even when it is invisible. But the marked difference in the temperature-coefficient of a glass vessel reduced to its final state by the clean-up and that of a vessel known to be metal coated is quite inconsistent with this explanation.

(4) *Permanence of the Clean-up.*

In this account one feature, common to the glass and the metal-coated vessels, has been left unnoticed. The low pressure produced in (*c*) by the clean-up is apparently permanent, so long as the vessel remains at room temperature; vessels re-examined a year after they were cleaned up have shown no increase of pressure in the interval of as much as 1 per cent. On the other hand, the heating in (*a*) reverses completely the effect of the clean-up; in the metal vessels or in the glass vessels in their final state, p_a is the same whether it is reached from p_b or from the much lower pressure p_c established at T_b by the clean-up. It may be asked, therefore, what temperature intermediate between T_a and T_b is necessary to reverse the clean-up.

There is no such definite temperature. When the cleaned-up vessel is heated, the pressure rises with the temperature more rapidly than it would if the same initial pressure had been established by mere cooling without the clean-up. If at any stage the heating is stopped and the vessel cooled, the pressure falls; if the heating has lasted a short time, or if the increase of temperature has been so small that p_b has never been reached, then the pressure on cooling, though higher than the initial p_c, will be less than p_b. But if it has been maintained for a sufficient length of time at any temperature at which pressure becomes greater than p_b, then the effect of the clean-up is wholly reversed and the pressure will fall on cooling to p_b, just as if the clean-up had never been performed.

If, however, the vessel is cleaned up at a temperature of 120° C., then the clean-up is not permanent; if the temperature is maintained the pressure rises slowly again to p_a. Accordingly, the permanence at room temperature is probably illusory. The truth is that the rate at which the clean-up is reversed increases rapidly with the temperature; at 20° C. it is to be measured in centuries, at 120° C. in hours. The labour of investigating the matter more nearly has therefore been judged prohibitive.

(5) *Nature of the Gas evolved.*

The experiments remaining to be recorded were directed to determine the nature of the residual gas. It was almost certainly not wholly the same in the blackened and in the unblackened vessels; for whereas in the former a thoriated tungsten filament would readily develop and maintain the high thermionic emission characteristic of thorium, in the latter the emission was never developed without "flashing" and never survived operation (*a*). But little more could be established definitely. The critical potentials of the residual gas were examined, absolute values being assigned by means of the ionization potential of Hg; only one such point could be identified certainly at the low pressures to which observations were necessarily confined; it varied irregularly between 15·8 and 17·2 volts. A comparison was made with vessels filled on the pump with H_2, CO_2, CO, H_2O. The last three gases all have critical potentials within this range, while that of hydrogen is less than 14·0 volts. The method would seem, therefore, to indicate that hydrogen is never present in considerable quantity, but this conclusion is so improbable that it seems rather to throw doubt on the validity of the method. Again, it was never possible to imitate exactly the current-voltage characteristic of the residual gas by means of any one of these gases alone. That gas is therefore probably a mixture—a conclusion likely enough, but one which makes it almost impossible to discover its composition by this method.

Attempts were also made to pump away and collect the residual gas. When a vessel is baked on the pump even to 120° C., the pressure in it is always notably higher than when it is cold; the evolution in these circumstances must be continuous. There is no difficulty in collecting gas from the high-pressure side of a diffusion pump connected to such a vessel, but there is great difficulty in proving that this gas comes entirely, or even mainly, from the baked vessel; some certainly comes from the connecting tubes (which cannot all be baked) and from the parts of the pump itself heated by the stream of mercury vapour. If, on the other hand, the gas is absorbed in cooled charcoal or even on cooled glass, there is very grave difficulty in ensuring that the gas liberated when the absorbent is heated is that which has been absorbed, neither more nor less. Much time was wasted on this work, and many methods which appeared satisfactory for a time had to be abandoned on further inquiry. The only conclusion that can be stated with confidence is, that in all experiments of this kind, water and carbon dioxide were always found in the gas collected, and both may therefore be present in the residual gas evolved from the heated vessel, while there was never certain evidence of the presence of any other gas from that source.

(6) *Discussion.*

Such are the facts; now some interpretation of them must be attempted. They are simplest when the vessels are metal coated. Here we may suppose that there is present in the vessel a definite quantity of gas, depending on the conditions prevailing during the deposition of the metal layers and on the maximum temperature to which it has since been heated. This gas is partially absorbed on the walls, the quantity so adsorbed increasing as the temperature falls. The clean-up increases this adsorption; its effect may be described, as in a previous paper [*], as a decrease of the vapour-pressure of the adsorbed gas, the decrease being strictly permanent only while the discharge lasts.

All this is comprehensible and in accordance with ideas already put forward. The only important question which remains is why the clean-up reduces the vapour-pressure. Here the later work has neither increased nor decreased the difficulties encountered previously. The ionization of the gas must cause it to assume some state in which it adheres more firmly to solid surfaces, but this state cannot be simply that of ionization.

---

[*] Research Staff of the G. E. C. *loc. cit.* p. 571.

But in the glass vessels the facts are not so simple. For here we have a truly permanent as well as a temporary effect of the clean-up. In the final state the conditions may be the same as in the metal-coated vessels; there may be a definite quantity of gas present of which merely the adsorption is changed. But if so, why is this quantity of gas so nearly independent of the history of the vessel and especially of the quantity initially present; if the clean-up can remove, gradually but permanently, so large a proportion of the initial gas, why can it not remove all? An answer may be suggested, athough it is admittedly speculative.

The permanent reduction of pressure must surely be due to some change in the state of the gas, involving the glass and possibly, though not certainly, the metal parts of the vessel, which is more permanent than adsorption; let us call it by that term of convenient ambiguity, a chemical reaction. It is conceivable that only part of the gas initially present is capable of this reaction, which ceases when that part is exhausted; but in view of the independence of the final on the initial pressure, another view seems much more probable. It is known * that some silicates at high temperatures in contact with water form water-silicate solutions characterized by definite equilibrium pressures of the vapour phase; it is not unlikely that similar solutions are formed in which carbon dioxide replaces water. There is abundant evidence that diffusion is possible in glass at temperatures as low as 120° C.; the glass is always in contact with water and carbon dioxide on the exterior surface; the equilibrium pressure of the saturated solutions of water and carbon dioxide in glass will therefore establish itself on the inside. This pressure at T_a may be identified with the final p_a. If there is initially within the vessel more vapour than corresponds to the pressure, the discharge, in addition to increasing the adsorption, as in metal vessels, will remove some of it permanently by the chemical reaction; but when the amount has reached that corresponding to the equilibrium pressure, any quantity removed by chemical reaction during (*c*) will be restored during the subsequent (*a*). On the other hand, p_b does not represent the equilibrium pressure at T_b for two reasons. First, the rate of diffusion doubtless increases enormously rapidly with the temperature; the temperature falls from T_a to T_b in a few minutes, and during this time diffusion has not time to establish equilibrium between the vapour phase and the interior of the glass. Second, since the pressure of the vapour on the outside of the vessel is much greater than that on the inside, the excess of vapour would not be transferred to the outside, even if infinite time were allowed; the superfluous vapour would remain inside as a separate phase; p_b represents the pressure exerted by this superfluous vapour after some of it has been adsorbed on the glass surface; owing to the adsorption p_b is less than p_a, but it will increase with T_a and p_a, even though T_b remains unchanged.

---

* G. W. Morey, J. Am. Chem. Soc. xxxix. p. 1173 (1917).

The objections to the theory are obvious. The complete similarity between samples of glass so different in composition is striking. Again, according to this view, the difference between the glass and the metal vessels is threefold. Metals do not enter into the supposed chemical reaction; they do not dissolve the gas; there is no diffusion through them. None of these differences are precisely what would be expected. Nor is it easy to get fresh confirmatory evidence. Of course an attempt might be made to prepare glass wholly free originally from dissolved gas and to prevent it from absorbing gas from the air by a vacuum jacket; but the experimental difficulties have so far deterred us from the attempt; it must be remembered that the supposed equilibrium pressure at 200° C. is only 10^{-4} mm., and that the pressure in the vacuum-jacket must be permanently below this limit. The only confirmation that can be offered at present is a difference in the time required to reach the equilibrium pressure at any given temperature; this time was distinctly less in the metal-coated vessels, a difference consistent with the view that in these diffusion within the walls plays no part.

(7) *Consequences for High Vacuum Technique.*

But whatever may be the explanation, there is no doubt that there is a difference between glass and metal-coated vessels, which may be most important for some practical purposes. Our observations indicate that it is impossible to make a vessel with bare glass walls in which the pressure will remain permanently as low as 10^{-6} mm. in such conditions as are likely to prevail in practice. The pressure can be reduced below this value by the clean-up; by taking great care to avoid heating of the walls of the vessel by the discharge used for the purpose, pressures as low as 10^{-8} mm.

can thus be reached; but a very moderate rise of temperature will restore the original value. On the other hand, by coating the walls with evaporated metal, and taking care that the pressure during the evaporation is as low as possible, it is quite easy to obtain vessels in which the pressure at 20° C. is permanently less than 10^{-7} mm. and not more than 10^{-6} mm. at 120° C.*

In fact, the impression prevailing in some quarters that metals are to be avoided in vessels in which the highest vacua are to be obtained, appears to be based on a misunderstanding. If metals are present, the gas on their surface adsorbed from the atmosphere must be removed (and also the gas in the interior if they are ever to be raised to a temperature at which this is likely to emerge). Now, this gas cannot be easily removed by baking the whole vessel, for a reason which these experiments disclose. The adsorption on a metal surface varies more rapidly with the temperature than that on a glass surface. When the vessel is hot, it will be filled with vapour coming from the glass; the supply of this gas is inexhaustible; and the resulting pressure at a given baking temperature depends mainly on the ratio of the area of the glass surface to the diameter of the tubes connecting the vessel to the pump. Unless this ratio is unusually small, the pressure in the vessel during baking at 400° will not be less than 10^{-4} mm., and usually will be considerably greater. As the vessel cools, this vapour tends to be adsorbed on the surface of the metal rather than that of the glass, and is evolved thence if the temperature of the metal rises in subsequent operations. The metal surface can be freed from gas only by making the metal hot while the glass is comparatively cold; but it can be freed by that method with great ease.

An illustration of this process is afforded by the difficulty mentioned on p. 373. There is always a rise of pressure when the filament of the gauge is heated, because the metal portions of it have adsorbed gas during the cooling of the vessel which is liberated when they are warmed by the filament. In the gauges in which this rise was abnormally large, the metal parts were probably in an abnormally receptive state, for some reason that is not understood at present.

---

* Even the smallest of these values are much greater than those which other workers appear to have no difficulty in obtaining. References to pressures of 10^{-9} are common in the literature, and even 10^{-13} has been mentioned; but it is never clear whether the vessels in which these pressures were found were sealed off from the pump.

APPENDIX.

The following table gives the chemical composition and some of the physical properties of the four glasses used in the experiments :—

Characteristics of Glasses used for Vessels.

		A.	B.	C.	D.
Chemical Composition (main constituents only)	SiO_2	56·5	62	72·0	72·0
	Al_2O_3	—	—	—	3·0
	PbO	30·0	20	—	—
	CaO	—	4	5·6	3·0
	MgO	—	—	3·0	—
	K_2O.........	5·2	9	1·0	4·6
	Na_2O	6·3	3	16·0	2·5
	B_2O_3	—	—	—	15·0
Softening temperatures (relative)......		420° C.	520° C.	550° C.	620° C.
Temperature at which resistivity is 10^7 ohm/cm.^{3}...........................		350° C.	415° C.	185° C.	400° C.
Temperature at which resistivity is 10^5 ohm/cm.^{3}		480° C.	550° C.	330° C.	605° C.

XXXI. *A Bath for Observations at Lower Temperatures.*

By W. H. PATTERSON [*].

A BATH of which the temperature is easily controllable, so that it can be rapidly cooled, then slowly cooled further, heated or kept constant near a particular temperature, is useful for many experiments.

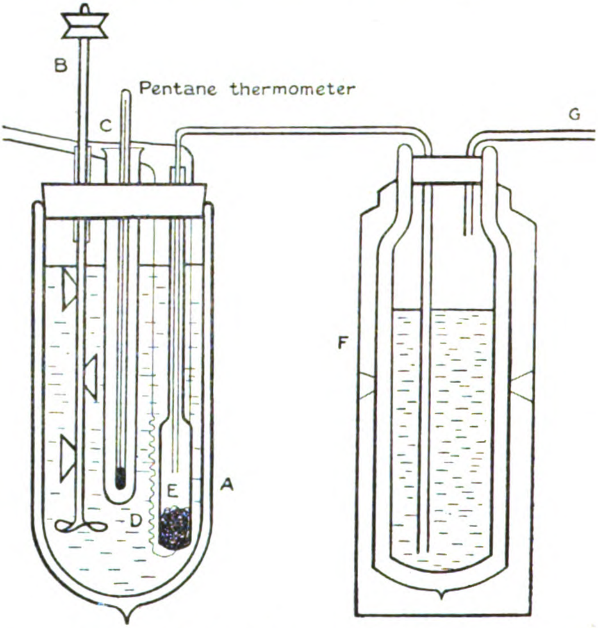
The apparatus described was designed for measuring the limits of miscibility of liquid pairs from room-temperature downwards. It has also been employed for determining "setting points" of many liquids, as a better control of purity than the tests usually made. In the latter case, the liquid to be tested is placed in the bath in a tube enclosed in a larger one with an air-space between, so that the pentane or other thermometer in the liquid may be sensible to the latent heat of change of state and indicate either the true "setting point," or, in the case of impure liquids, the "setting point range." While no novel principle is involved [†], the apparatus is simple, it has a wide range, and even at the higher temperatures has many advantages over the use of ice or salt mixtures. It consists of a Dewar flask A, 11 × 4·5 cm., nearly filled with alcohol and provided with a cork through which pass a mechanical stirrer B and the tube for liquids to be tested C.

---

[*] Communicated by the Author.

[†] d'Arsonval, *C. R.* 133. p. 980 (1901), used a bath of paraffin cooled by allowing liquid air to drop into, and evaporate from, a small metal vessel placed on the surface, for maintaining temperatures −115° to −194° C.

Connexions are made through the cork to a coil of about 50 cm. No 26 Eureka wire (the electrical resistance of which changes but little with the temperature). When the ends of the coil are connected to a single accumulator the rise of temperature of the bath is about 1°·5 per minute. A two-way switch is provided for slower heating.



The cooling is effected by means of the tube E, which is wider at the lower end. At the bottom is a wad of cotton-wool. Into this tube passes a narrow glass tube with a fine orifice leading from the Dewar flask F which contains liquid air. The liquid air, in small amounts, is forced into E at will by means of a bicycle pump at G.

The apparatus has been used for temperatures between +30° and −120° C. A steady temperature is attained within half a minute of breaking the current or forcing over the liquid air. The temperature can be reduced, if desired, by 100 degrees in 15–20 minutes. Observations of the thermometer and liquids tested can readily be made through the walls of the Dewar flask, and it is only necessary to wipe off the moisture condensed on the outside occasionally, even at the lowest temperatures. The use of liquid air in the way described is very economical.

XXXII. *Molecular Association and the Equation of State.*

By M. F. CARROLL, *M.Sc.* (*Lond.*)*.

IN a recent paper by Prof. J. R. Partington and the author on the "Specific Heats of Carbon Monoxide and Hydrocyanic Acid Vapour"†, it was assumed from the measurements of Usherwood that hydrocyanic acid vapour is considerably associated to double molecules at the temperatures and pressures employed by Usherwood ‡ and the authors. Further, it was deduced that in the neighbourhood of the critical point, hydrocyanic acid consists almost entirely of double molecules; and since the critical constants of this compound have not yet been determined, use was made of certain empirical relations given by Walden § for calculating the critical data. Walden distinguishes between the so-called "normal" substances (such as hydrocarbons, ethers, etc.) and those described as "abnormal" (such as water, ammonia, acetic acid, and the alcohols), on the ground that certain physical properties of the "normal" compounds bear a simple and constant relation to each other, while the "abnormal" compounds show considerable divergence from this rule.

Similar evidence for this differentiation between "normal" and "abnormal" substances may be found in the variation of the constant f of van der Waals' vapour-pressure equation

$$\log P_c/p = f(T_c/T-1),$$

where f varies from about 1·8 to 4·0 for different substances. Thus in Landolt-Börnstein's tables the following classification is adopted:

Group 1. $f < 2{\cdot}5$, $RT_c/P_cV_c = 3{\cdot}0$ to $3{\cdot}5$

Group 2. $f = 2{\cdot}6$ to $3{\cdot}2$, $RT_c/P_cV_c = 3{\cdot}5$ to $4{\cdot}0$

Group 3. $f > 3{\cdot}2$, $RT_c/P_cV_c > 4{\cdot}0$,

where f is defined above and RT_c/P_cV_c is the ratio of the ideal to the actual value of RT at the critical point. Group 1 comprises the permanent gases, Group 2 the

---

* Communicated by the Author.

† Phil. Mag. xlix. p. 655 (1925).

‡ Journ. Chem. Soc. (T), ccxi. p. 1604 (1922).

§ *Zeit. phys. Chem.* lxvi. p. 385 (1909).

"normal" substances, and Group 3 the "abnormal" substances. Another criterion of abnormality is Trouton's rule,

$$\lambda / T = \text{a constant} = c,$$

where λ is the molecular latent heat of evaporation and T the absolute temperature. The constant c is approximately equal to 21·0 cals./deg. for the "normal" substances, and substances giving a higher value for c are regarded as associated, although acetic acid and its homologues, which are undoubtedly associated to a large extent, give a very low value for c, while a further class of substances corresponding to Group 1 of the above table, and which we will refer to as "subnormal" substances," give a very low value of c, ranging from 12·0 to 17·0 cals./deg.

The strongest evidence for this arbitrary division is found in the rule of Eötvös as modified by Ramsay and Young. The latter authors have shown that, in order to account for the deviation from the equation

$$d\,.\,\gamma\,\frac{(Mv)^{2/3}}{dt} = \text{a constant} = -2\cdot 11 \text{ approx.},$$

a greater molecular weight must be assigned to the "abnormal" substances than that obtained from vapour-density measurements. This equation is derived on the assumption that the "normal" substances are quite unassociated in the liquid state. Of late, however, this assumption has been questioned, although it appears to be generally accepted. A closer survey of the physical properties of the "normal" and "abnormal" substances shows that the division is quite arbitrary, the line of demarcation being very indefinite.

An attempt will now be made to show that association is common to all substances, and is quite appreciable even in the case of the gases of the inert group at low temperatures and high pressures. Although water and the alcohols are regarded as associated in the liquid state, it is usually assumed that in the gaseous state they are unassociated. This view is illogical, as may readily be seen from a consideration of the Cailletet-Mathias density-temperature curve. Thus, starting from water at its boiling-point and proceeding along the liquid-density curve, we should expect to find as the curve approaches the critical point that the degree of association becomes progressively less, since the volume increases. In the case of association to double molecules, the dependence of α, the degree of association, upon the volume is given by the equation

$$\frac{\alpha^{\frac{1}{2}}V^{\frac{1}{2}}}{(1-\alpha)} = K,$$

where K is the association constant. Since the change is perfectly continuous, as is also the change from liquid to vapour at the critical point, we may reasonably assume that α decreases progressively with increase of volume; and proceeding thence along the vapour-density curve, we see that association should exist in the vapour at the boiling-point, or indeed under any conditions, and would in certain cases be given quantitatively by the above equation.

The only methods available for the absolute determination of association are a measurement of the vapour density of the gas and the various methods for estimating the molecular weight of dissolved substances. Only those substances are regarded as associated in the gaseous state which, like acetic acid and its homologues, give a vapour density considerably greater than the theoretical. Variations in the vapour densities of other substances are ascribed to deviation from the gas laws, and are accounted for by introducing into the ideal gas equation some function of P or V which will account for these deviations. So far all these equations of state, although showing good agreement in particular cases, are incapable of general application; so that of all the equations devised, whether theoretical or empirical, not one can be used to represent accurately the behaviour of fluids in general, or even that of any particular fluid over the entire range of its existence. If, however, molecular association is assumed to be quite general, it will be obvious that no known equation of state can represent accurately the behaviour of actual fluids. With regard to liquids, it appears to be still assumed quite generally that the molecular weight of a substance in the liquid state is necessarily the same as in the gaseous state—an assumption which is clearly unjustified. Such evidence as exists in its favour depends on the further assumption that the molecular weights of certain "normal" substances are identical under all conditions. The difficulty in establishing the existence of association in the vapours of the "normal" substances lies in the fact that the degree of association is so small that its effect on the vapour density is obscured by experimental error and by deviations from the gas laws. It should, however, be capable of approximate determination—provided sufficient accuracy can be obtained in the vapour density measurements—by the use of a suitable equation of state which would represent exactly the deviations from the gas laws of an ideally "normal" substance—that is, a substance which possesses the same molecular weight under all conditions.

The Equation of State.

A discussion of the relative merits of the many equations of state which have been put forward from time to time is unnecessary in view of the attention which the subject has already received, and, in any case, only a few of these equations possess any real physical significance. Any equation purporting to account for the deviation of actual fluids from the ideal gas equation $PV=RT$ must take into consideration

(1) the attraction existing between the molecules ;
(2) the finite size of the molecules;
(3) the finite time of contact.

The latter does not appear to have received the attention that it merits, but the effect of (1) and (2) has been treated exhaustively in most of the equations of state put forward, and of these the equation of van der Waals,

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT,$$

is from the theoretical point of view the most attractive.

Applying the usual methods for the solution of this equation at the critical point, we find $RT_c/P_cV_c=s=8/3$ for all substances. The main objections to this equation are that a and b are not quite constant, and s is not constant and equal to 8/3, but varies from 3·1 for helium to about 5·0 for acetic acid. This variation is undoubtedly outside the range of experimental error, in view of the substantial agreement obtained by different observers for any given substance. This fact has been recognized by Guye, who expressed s as a function of the critical temperature, and other observers have modified the equation of state to allow for this and other variations. The conception of general association offers an explanation of this variation, as will be shown later.

The basic assumption made in the present theory is that the discrepancy between van der Waals' equation as applied to actual fluids and the true equation of state depends entirely upon *association*, and that for a completely non-associated substance van der Waals' equation holds rigidly—that is, a and b are constant and $s=8/3$. Association is defined in a very broad sense. Thus, if we consider the effect of (3) from the standpoint of statistical dynamics, it will be obvious that the time of contact determines the number of molecules in a given volume. If the time of contact is not zero, it is possible that the substance is associated in the chemical sense (chemical combination) and groups of molecules are in contact for relatively long periods, or that the time of contact is small but finite, and oscillations about a centre of mass may occur before the molecules separate. This difference is clearly one of degree rather than of kind; hence both effects are included under the term "association." An ordinary substance, therefore, may be considered as an equilibrium mixture of unassociated molecules with the various products of association. If the degrees of association to 2, 3, or 4 molecules etc. are respectively α, β, γ, etc., one gram-molecule of an unassociated substance will give $(1-\alpha-\beta-\gamma-\ldots)$ unassociated molecules and $\left(\frac{\alpha}{2}+\frac{\beta}{3}+\frac{\gamma}{4}+\ldots\right)$ associated molecules. Therefore the number of molecules in equilibrium will be $\left(1-\frac{\alpha}{2}-\frac{2\beta}{3}-\frac{3\gamma}{4}-\ldots\right)$. The constant R of van der Waals' equation is proportional to the mean kinetic entropy of the molecules and is purely additive; hence, if R' is the absolute gas constant referred to N (Avagadro's constant) individual molecules,

$$R = R'\left(1-\frac{\alpha}{2}-\frac{2\beta}{3}-\frac{3\gamma}{4}-\ldots\right) = \frac{R'}{x},$$

where x is the ratio of the actual to the theoretical number of molecules. At the crit'cal point this relation alone determines x for

$$\frac{R'}{x}\cdot\frac{T_c}{P_cV_c} = \frac{8}{3} \quad \text{and} \quad \frac{R'T_c}{P_cV_c} = s,$$

and therefore $x=3/8s$.

It is not possible to state so precisely the effect of association on a the constant of molecular attraction, or on b the limiting molecular volume; but in general we may write

$$a = a'f_1(\alpha, \beta, \gamma, \ldots) \quad \text{and} \quad b = b'f_2(\alpha, \beta, \gamma, \ldots),$$

postulating only that a' and b' are constants and that the functions $f_1(\alpha, \beta, \gamma, \ldots)$ and $f_2(\alpha, \beta, \gamma, \ldots)$ involve no other variable than $(\alpha, \beta, \gamma, \ldots)$. The modified van der Waals' equation then becomes

$$\left[P + \frac{a'}{V^2}\cdot f_1(\alpha, \beta, \gamma, \ldots)\right]\left[V - b'f_2(\alpha, \beta, \gamma, \ldots)\right]$$
$$= f_3(\alpha, \beta, \gamma, \ldots)R'T.$$

If for simplicity we confine ourselves to association to double molecules, we have

$$\left[P+\frac{a'}{V^2}\cdot f_1(\alpha)\right]\left[V-b'f_2(\alpha)\right]=\left(1-\frac{\alpha}{2}\right)R'T.$$

Following van Laar, we have for a and b

$$a=\left[a'(1-\alpha)^2+\sqrt{a'a''}\,.\,2\alpha(1-\alpha)+a''\alpha^2\right],$$

$$b=b'(1-\alpha)+b''\frac{\alpha}{2}.$$

The first expression may be more conveniently written

$$a=\left[\sqrt{a'}(1-\alpha)+\sqrt{a''}\frac{\alpha}{2}\right]^2,$$

where a' and b', a'' and b'' are the constants for the unassociated and associated molecules respectively. The simplest assumption we can make with regard to these constants is that $a''=2a'$ and $b''=\sqrt[3]{2b'}=b'/{\cdot}631$, which gives for all substances

$$a=a'(1-{\cdot}293\alpha)^2 \quad \text{and} \quad b=b'(1-{\cdot}369\alpha).$$

These expressions are probably too simple, and may vary with the nature of the substance. Quite good results have been obtained by their use, however, as will be shown later. Applying the usual methods for the evaluation of the constants of the equation in terms of the critical constants, we find

$$a'=\frac{a}{f_1(\alpha)}=\frac{3P_cV_c^2}{(1-{\cdot}586\alpha+{\cdot}086\alpha^2)},$$

$$b'=\frac{b}{f_2(\alpha)}=\frac{V_c}{3(1-{\cdot}369\alpha)},$$

and

$$\frac{\left(1-\frac{\alpha}{2}\right)R'T_c}{P_cV_c}=\frac{8}{3}, \quad \text{or} \quad \frac{R'T_c}{P_cV_c}=s=\frac{8\left(1-\frac{\alpha}{2}\right)}{3},$$

from which α and therefore a' and b' may be calculated. The values of α, a', and b' calculated from the critical data are given in Table I. Columns 2 to 4 contain the most recent values of the critical data given in Landolt-Börnstein's tables. Column 5 contains the value of s, and columns 6 to 8 the values of α_c, a', and b' calculated therefrom. Column 9 contains the values of the association constant K_c given by the expression

$$K_c=\frac{\alpha_c^{\frac{1}{2}}V_c^{\frac{1}{2}}}{(1-\alpha_c)}.$$

Column 10 contains the ratio of the limiting volume to the

TABLE I.

Substance.	T_c° abs.	P_c. atmos.	V_c. c.c.s.	s.	a.	$a' \times 10^{-6}$.	b'. c.c.s.	K_c.	b''/V_c.
Hydrogen	33·2	12·8	69·68	3·038	·244	·2165	25·53	5·46	·231
Helium	5·2	2·3	61·55	3·082	·269	·0282	22·80	5·57	·233
Argon	150·7	50·0	75·15	3·293	·380	1·074	29·13	8·62	·244
Nitrogen	126·0	33·5	90·07	3·431	·445	1·076	35·91	11·42	·251
Oxygen	154·9	49·7	74·42	3·437	·448	1·095	29·72	10·47	·252
Methane	190·2	45·6	98·56	3·473	·464	1·783	39·63	12·62	·253
Carbon monoxide	134·4	34·6	90·03	3·542	·494	1·152	36·67	13·19	·257
Xenon	289·7	58·2	113·2	3·611	·522	3·268	46·77	16·10	·261
Carbon dioxide	304·4	72·9	94·84	3·615	·525	2·751	39·22	14·86	·261
Sulphur dioxide	430·2	77·7	124·7	3·646	·537	5·109	57·82	17·68	·262
Carbon tetrachloride	556·3	45·0	276·2	3·675	·548	14·65	115·3	27·22	·263
i-Pentane	460·9	32·9	307·3	3·741	·574	13·52	129·9	31·23	·266
Benzene	561·6	47·9	256·2	3·759	·581	13·72	108·6	29·12	·267
n-Pentane	470·3	33·0	309·8	3·771	·585	13·87	131·7	32·49	·267
Fluor-benzene	559·7	44·6	271·4	3·797	·595	14·48	116·0	31·37	·269
Ethyl ether	466·9	35·6	281·9	3·819	·603	12·54	120·8	32·86	·270
Methyl acetate	506·8	46·3	227·5	3·948	·645	10·96	99·5	34·13	·271
Ethyl acetate	523·2	38·0	286·1	3·952	·650	14·28	123·7	39·01	·272
Nitric oxide	177·1	64·0	57·25	3·966	·655	·967	25·17	17·76	·277
Ethyl alcohol	516·2	63·0	167·0	4·029	·676	8·179	74·22	32·29	·280
Ammonia	405·6	112·3	71·91	4·124	·707	2·733	32·44	24·32	·284
Methyl alcohol	513·0	78·5	117·6	4·563	·832	5·707	56·57	58·57	·303
Water	638·0	200·5	54·71	4·784	·885	2·751	27·04	60·46	·311

critical volume, a value which increases with the degree of association. Assuming that association only takes place to double molecules, the limiting volume is therefore equal to the volume of the double molecules, which is found by putting $\alpha=1$ in the expression given on p. 390, whence

$$b''=\cdot631b' \quad \text{and} \quad \frac{b''}{V_c}=\frac{\cdot631b'}{V_c}=\frac{1}{3}\cdot\frac{\cdot631}{(1-\cdot369\alpha_c)}.$$

The mean value from Table I. is approximately ·260, which is the value obtained by D. Berthelot * by extrapolating the Cailletet-Mathias mean density line to the absolute zero. No great reliance can be placed on this criterion, however, since we are in doubt as to the validity of the extrapolation, and, besides, we have no reason to assume that all substances are completely associated at the absolute zero. Indeed, conceding the first point, we may explain the variation in the values of b''/V_c by assuming that the simpler substances are less completely associated, and the more complex substances are further associated to triple molecules etc. at the absolute zero.

Table I. contains only those values of the critical constants for which reasonable agreement has been obtained by different observers, and it is assumed for the sake of comparison that association only proceeds to the second stage, which, as will be shown later, is not strictly true, especially in the case of the "abnormal" substances. The examples given in the table may be divided roughly into the three classes mentioned above—from hydrogen to carbon monoxide "subnormal," from xenon to ethyl acetate "normal," and from nitric oxide to acetic acid "abnormal" substances; but, as previously pointed out, this division is purely arbitrary, as will be seen by following the values of s from ethyl ether to methyl alcohol and observing the gradual transition from "normal" to "abnormal" substances.

Young's work, from which most of the data are taken, was mainly confined to the "normal" substances, the physical properties of which fall within very narrow limits—a fact which has given rise to many empirical relations which are entirely unsuccessful outside this range.

The equation of state can now be used to calculate the degree of association in both the liquid and gaseous state at any temperature and pressure. Thus, on any given isotherm,

---

* *Arch. Neer.* (2) v. p. 466 (1900).

since the association constant K_v is a function of temperature only, it should be constant for all values of P and V on the isotherm. Tables II. to IV. contain the values of α and K_v calculated for some representative substances. The degree of association was calculated by substituting successive values of α in the equation of state until a value which satisfied the equation was found. The value of the association constant was then calculated, assuming that the law of mass action holds under these conditions.

TABLE II.

Hydrogen *.

$T = 273°$ abs. $a' = 2{\cdot}165 \times 10^5$. $b' = 25{\cdot}53$ c.c.s.

P atmos.	V c.c.s.	α.	K_v.
100	239·6	·0184	2·14
150	164·4	·039	2·64
200	127·4	·056	2·83
400	71·9	·134	3·58
600	53·48	·216	4·34
800	44·21	·290	4·98
1000	38·56	·363	5·87

TABLE III.

Carbon Dioxide *.

$a' = 2{\cdot}751 \times 10^6$. $b' = 39{\cdot}22$ c.c.s.

$T = 323°$ abs.				$T = 373°$ abs.			
P atmos.	V c.c.s.	α.	K_v.	P atmos.	V c.c.s.	α.	K_v.
50	421·5	·170	10·10	50	540·9	·061	6·12
100	110·1	·387	10·64	100	230·9	·132	6·36
125	70·84	·454	10·41	125	169·8	·165	6·34
150	62·62	·467	10·25	150	131·2	·191	6·19
200	56·06	·480	9·97	200	91·33	·241	6·18
400	47·72	·487	9·40	400	58·19	·345	6·84
600	44·34	·494	9·25	600	51·01	·381	7·12
1000	40·66	·520	9·58	1000	44·82	·428	7·65

---

* Amagat, *Ann. Chim. Phys.* (5) xxix. p. 68 (1898).

TABLE IV.

Ethyl Ether *.

$a' = 1{\cdot}254 \times 10^7$. $b' = 120{\cdot}8$ c.c.s.

$T = 470^\circ$ abs.

P atmos.	V c.c.s.	a.	K_v.
13·29	2454	·156	23·16
11·80	2817	·143	23·42
9·62	3540	·128	24·41
8·114	4262	·116	25·16
7·049	4982	·1028	25·23
6·207	5702	·0930	25·40
5·551	6419	·0905	26·51
5·027	7137	·0852	26·96

It will be seen from the above tables that fairly good agreement is obtained for carbon dioxide and ether, but the value of K_v for hydrogen shows a marked variation. Closer agreement can hardly be expected in view of the inaccuracies inherent in the determination of the critical data on which are based the values of a' and b', and consequently the values of α and K_v. The small differences in the results for the critical constants obtained by different observers are sufficient to cause appreciable error in the value of α; hence the exact application of the equation of state must depend on very accurate determinations of the critical data.

The equation of state can also be used to calculate the value of α and K_v on the vapour-pressure curve for both the liquid and gaseous phases. At any given point on the curve, K_v should be identical for both phases, or

$$\frac{\alpha_g^{\frac{1}{2}} V_g^{\frac{1}{2}}}{(1-\alpha_g)} = \frac{\alpha_l^{\frac{1}{2}} V_l^{\frac{1}{2}}}{(1-\alpha_l)} = K_v.$$

The values of α and K_v on the vapour-pressure curve for various substances have been calculated, and a selection of the results are given in Tables V. to VIII. The degree of association-temperature curve for carbon tetrachloride and isopentane has been plotted, and is shown in the accompanying diagram.

---

* Ramsay & Young, Phil. Mag. xxiii. p. 435 (1877).

Fig. 1.—Degree of Association-Temperature.

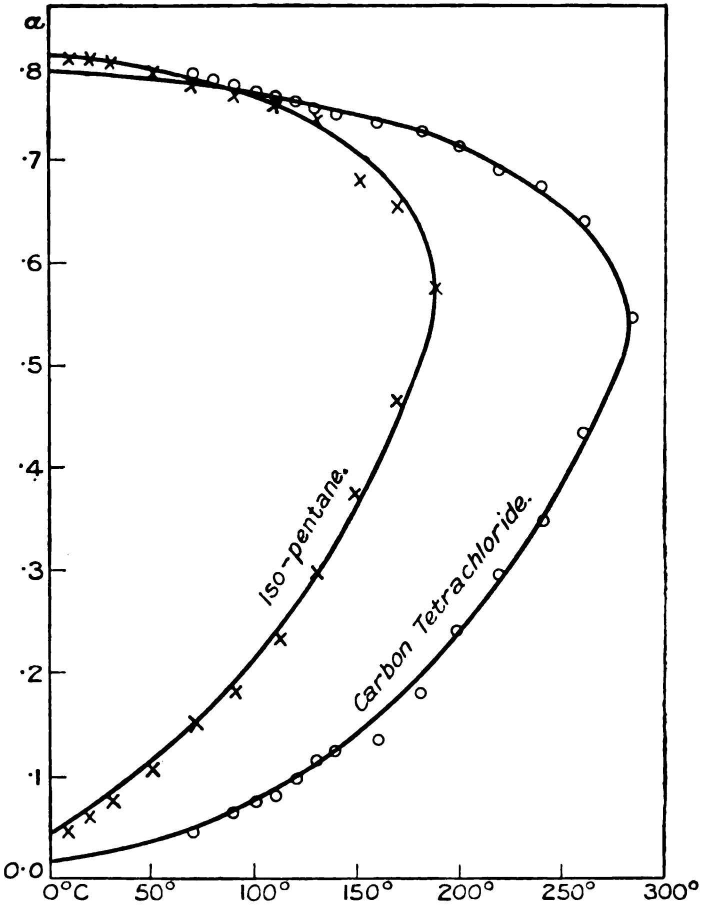


TABLE V.

Carbon Dioxide *.

$a' = 2·751 \times 10^6$. $b' = 39·22$ c.c.s.

$T°$ abs.	P atmos.	V_l c.c.s.	V_g c.c.s.	a_l.	a_g.	K_l.	K_g.
273	34·3	48·15	458·2	·672	·293	17·34	16·39
278	39·0	49·56	346·8	·661	·336	16·89	17·15
283	44·2	51·40	330·9	·651	·352	15·58	16·65
288	50·0	54·06	278·5	·630	·387	15·75	16·93
293	56·3	57·45	231·6	·611	·420	15·21	17·00
298	63·3	62·59	183·3	·578	·470	14·33	17·52
303	70·7	73·58	131·7	·541	·514	13·75	16·93
304·4	72·9	94·84		·525		14·86	

---

* Amagat, *loc. cit.*

TABLE VI.

Benzene *.

$a' = 1{\cdot}372 \times 10^7$. $b' = 108{\cdot}6$ c.c.s.

$T°$ abs.	P atmos.	V_l c.c.s.	V_g c.c.s.	a_l.	a_g.	K_l.	K_g.
343	·511	94·58	38230	·817	·0234	48·03	30·65
353	·992	95·76	28550	·814	·0228 ?	47·46	26·20
363	1·337	96·94	21610	·811	·0302	46·91	26·34
373	1·769	98·40	16580	·808	·0456	46·44	28·81
393	2·944	101·4	10160	·795	·0868	43·80	32·53
423	5·705	106·7	5429	·777	·120	40·83	28·97
443	8·387	110·9	3737	·770	·144	40·17	27·07
473	14·03	118·3	2200	·752	·213	38·00	27·51
503	22·13	128·6	1305	·724	·314	34·96	29·51
533	33·39	146·4	754·4	·675	·444	30·59	32·92
561·6	47·9	256·2		·581		31·23	

TABLE VII.

Carbon Tetrachloride †.

$a' = 1{\cdot}465 \times 10^7$. $b' = 115{\cdot}3$ c.c.s.

$T°$ abs.	P atmos.	V_l c.c.s.	V_g c.c.s.	a_l.	a_g.	K_l.	K_g.
343	·808	102·9	33700	·782	·0425	41·14	39·53
353	1·110	104·3	25310	·777	·0316 ?	40·37	— ?
363	1·463	105·8	19330	·772	·0630	39·65	37·27
373	1·917	107·4	15000	·766	·0746	38·75	36·23
383	2·479	109·0	11790	·760	·0838	37·93	34·31
393	3·147	110·8	9396	·756	·0992	37·51	33·89
403	3·950	112·6	7560	·750	·1136	36·76	33·07
413	4·901	114·5	6160	·746	·1250	36·39	31·61
433	7·288	118·6	4319	·737	·1362	35·55	27·75
453	10·40	123·5	2941	·728	·180	34·85	28·02
473	14·39	129·5	2075	·714	·241	33·62	29·46
493	19·47	137·3	1481	·692	·295	31·64	29·65
513	25·83	147·4	1052	·674	·350	30·59	29·52
533	33·58	163·7	717·6	·639	·434	28·35	31·18
556·3	45·0	276·2		·548		27·22	

---

* Young, Proc. Roy. Soc. Dubl. (n. s.) xii. p. 374 (1910).
† Young, *loc. cit.*

TABLE VIII.

Isopentane *.

$a' = 1{\cdot}352 \times 10^7$. $b' = 129{\cdot}9$ c.c.s.

T° abs.	P atmos.	V_l c.c.s.	V_g c.c.s.	α_l.	α_g.	K_l.	K_g.
283	·514	114·4	43700	·800	·0450	47·84	46·44
293	·754	116·2	30530	·797	·0594	47·67	45·28
303	1·073	118·1	21810	·793	·0782	46·49	45·34
323	2·017	122·4	12070	·784	·1068	44·42	40·19
343	3·489	127·3	7120	·773	·1502	43·72	38·50
363	5·563	133·0	4453	·765	·1814	42·92	34·72
383	8·679	140·1	2865	·754	·234	41·78	33·79
403	12·77	149·1	1879	·741	·297	37·04	34·43
423	18·17	162·0	1234	·680	·371	32 80	34·02
443	25·13	184·0	771·1	·654	·464	31·71	35·29
461	32·96	307·3		·574		31·22	

Quite good results are obtained for carbon tetrachloride, carbon dioxide, and isopentane; but the divergence due to further association becomes appreciable in the case of benzene, ether, and alcohol, the latter giving a value of $\alpha = {\cdot}92$ at the boiling-point, assuming simple association only. With water and acetic acid the effect of further association is more marked, and on calculating the degree of association for these substances on the above assumption a value of $\alpha > 1{\cdot}0$ is obtained. Attempts to evaluate the first and second degree of association α and β for these substances present considerable difficulties, but approximate methods of calculation give for water a value of $x = 2{\cdot}3$ and for acetic acid $x = 3{\cdot}0$ at the boiling-point. It is probable also that association proceeds to the second stage even in the case of the simpler compounds given above, but the effect is relatively small and does not cause any serious error below $\alpha = {\cdot}70$. Above this the effect of further association becomes apparent. It is for this reason that such emphasis has been placed on the results for carbon tetrachloride, the simplest of the thirty organic compounds investigated by Young. The degree of association of this compound is only ·548 at the critical point, and the values of K_l and K_g show very good agreement. The effect of discrepancies in the experimental data is seen in Table VII. The vapour-pressure of carbon tetrachloride at 353° abs. is not given in Young's paper; hence the value given by Regnault † was used instead. The divergence is quite marked, as will be seen from the value of α at this

---

* Young, *loc. cit.*

† *Mém. des Paris*, xxvi. p. 339 (1860).

temperature. As would be expected, the values of K show a more regular decrease than the values of K_g, since a determination of the volume of the vapour is attended by greater difficulties and is more liable to error than a determination of the volume of the liquid. Also the value of α_l is not so seriously affected by inaccuracies in the vapour-pressure determination as is the value of α_g. Hence, in the calculation of the heat of association Q_v, only the values of K_l have been used. In the case of carbon dioxide the temperature range is too small to give even an approximate estimate of the heat of association; but good agreement is obtained for the other examples given above if the values of α_l are used and Q_v calculated over a temperature range of at least 100° C. Table IX. contains the values of Q_v for carbon tetrachloride calculated from the formula

$$Q_v = 4{\cdot}571 \log_{10} \frac{K_1}{K_2} \cdot \frac{T_2 T_1}{T_2 - T_1}$$

over the temperature range stated.

TABLE IX.

Temperature range, ° abs.	Q_v cals.	Mean Q_v cals.
343–443	478·2	478·4
353–453	467·0	
363–463	467·7	
373–473	497·5	
383–483	481·0	

As in the above table, Q_v is fairly constant for all the substances investigated between the boiling-point and the critical point; but a slight increase with temperature is shown and is to be expected, since, in general, Q_v is a function of the absolute temperature. No attempt has been made to allow for this variation, as the values of K_l are not considered to be sufficiently accurate to admit of more exact calculation.

In all cases investigated up to the present it has been found that Q_v increases with temperature, but is approximately constant and equal to 500 cals. for the "normal" substances between the boiling-point and the critical point. For the "subnormal" substances it is very much less: *e.g.* for nitrogen, $Q_v = 79$ cals. In general, Q_v increases with the complexity of the molecule.

The Latent Heat of Evaporation.

A further test of the equation of state consists in the calculation of the latent heats of evaporation from values of P and V on the vapour-pressure line.

Maxwell's theorem gives the relation *

$$P(V_g - V_l) = \int_{V_l}^{V_g} p \, . \, dV. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Substituting in the equation the expression for p derived from the equation of state, we have

$$\int_{V_l}^{V_g} p \, . \, dV = \int_{V_l}^{V_g} \frac{\left(1-\frac{\alpha}{2}\right) RT}{(V-b)} \, . \, dV - \int_{V_l}^{V_g} f_1(\alpha) \, \frac{a'}{V^2} \, . \, dV \quad (2)$$

$$= \int_{Vl}^{V_g} \frac{R'T}{V-b} \, . \, dV - \int_{V_l}^{V_g} \frac{\alpha R'T}{2V} \, . \, dV$$

$$- \int_{V_l}^{V_g} \frac{a'}{V^2} f_1(\alpha) \, . \, dV. \quad . \quad . \quad (3)$$

Neglecting the variation of b with α, and substituting dV in terms of α,

$$dV = K^2 \frac{(\alpha^2 - 1)}{\alpha^2} d\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\therefore \int_{V_l}^{V_g} p \, . \, dV = \int_{V_l}^{V_g} \frac{R'T}{V-b} \, . \, dV + \int_{\alpha_l}^{\alpha_g} \frac{R'T}{2} \, . \, \frac{1+\alpha}{1-\alpha} d\alpha$$

$$+ \frac{a}{K^2} \int_{al}^{\alpha_g} \frac{1+\alpha}{(1-\alpha)^3} \, . \, (1 - {\cdot}586\alpha + {\cdot}086\alpha^2) \, d\alpha, \quad . \quad (5)$$

which gives on integration the expression :

$$P(V_g - V_l) = R'T \left[\log \frac{(V-b)_g}{(V-b)_l} - \log \frac{(1-\alpha)_g}{(1-\alpha)_l} + \frac{\alpha_l - \alpha_g}{2} \right]$$

$$+ \frac{a}{K^2} \left[\frac{1}{2} \left(\frac{1}{(1-\alpha_l)^2} - \frac{1}{(1-\alpha_g)^2} \right) - {\cdot}328 \left(\frac{1}{(1-\alpha_l)} \right. \right.$$

$$\left. \left. - \frac{1}{(1-\alpha_g)} \right) + {\cdot}242 \log \frac{(1-\alpha)_g}{(1-\alpha)_l} \right] \quad . \quad . \quad . \quad . \quad (6)$$

From the Clausius-Clapeyron equation,

$$\lambda = T \frac{dP}{dT} (V_g - V_l),$$

$$\lambda = R'T \left[\log \frac{(V-b)_g}{(V-b)_l} - \log \frac{(1-\alpha)_g}{(1-\alpha)_l} + \frac{\alpha_l - \alpha_g}{2} \right]$$

$$+ \frac{2aQ_v}{K^2 R'T} \left[\frac{1}{2} \left(\frac{1}{(1-\alpha_l)^2} - \frac{1}{(1-\alpha_g)^2} \right) \right.$$

$$\left. - {\cdot}328 \left(\frac{1}{(1-\alpha_l)^2} - \frac{1}{(1-\alpha_g)^2} \right) + {\cdot}242 \log \frac{1-\alpha_g}{1-\alpha_l} \right], \quad . \quad (7)$$

on differentiating the expression for $P(V_g - V_l)$ with respect to T.

---

* *Cf.* Partington, 'Chemical Thermodynamics,' 1st edit. pp. 231, 349.

From this expression, λ can be calculated and compared with the value obtained experimentally and with the value calculated from the vapour-pressure equation. In the differentiation of (6), Q_v has been assumed constant, whereas, as previously pointed out, it varies with the temperature. It would have been more accurate to have used the expression

$$Q_v = Q_0 - aT.$$

This, and the assumptions involving the term $(V-b)$, account for the discrepancies between the calculated and experimental results. The results for carbon tetrachloride and benzene are given in the following tables:—

TABLE X.

Carbon Tetrachloride.

$Q_v = 478{\cdot}2$ cals. $a' = 1{\cdot}465 \times 10^7$.

T° abs.	a_l.	a_g.	K_l.	λ cals.	λ cals. (Young).
343	·782	·0425	41·14	7450	7210
353	·777	·0316	40·37	7200	7090
363	·772	·0630	39·65	7010	6955
373	·766	·0746	38·75	6800	6800
393	·756	·0992	37·51	6400	6479
413	·746	·125	36·39	5980	6148
433	·737	·136	35·55	5570	5843
453	·728	·180	34·85	5150	5451
473	·714	·241	33·62	4740	5020

TABLE XI.

Benzene.

$Q_v = 618{\cdot}8$ cals. $a' = 1{\cdot}372 \times 10^7$.

T° abs.	a_l.	a_g.	K_l.	λ cals.	λ cals. (Young).
363	·811	·0302	46·91	7870	7310
373	·808	·0456	46·44	7560	7130
393	·795	·0868	43·80	7035	6760
423	·777	·120	40·83	6470	6300
473	·752	·213	38·00	5330	5368

Empirical Relations.

A comparison of the value of x—the ratio of the actual molecular weight to the ideal molecular weight—at the boiling-point shows that, as far as can be determined at present, the ratios x_g/x_c and x_l/x_c are approximately constant for all substances. In other words, the law of corresponding states applies also to the degree of association. Hence any law or rule which has for its basis the law of corresponding states should also include some reference to the degree of association. Thus, with Trouton's rule, the "normal" substances which give a constant approximately equal to 21·0 cals./deg. are precisely those which have approximately the same reduced molecular volume and molecular ratio x at the boiling-point, and the other constants in the latent heat equation (7) are also approximately equal. Therefore Trouton's rule should be modified to include some function of α. In this connexion it is interesting to note that Longuinine * shows that, if in the case of the fatty acids the double molecular weight is used in calculating $\lambda = ML$, the same value is obtained for the constant in Trouton's expression as for the "normal" substances. This may be expressed by writing

$$\frac{\lambda}{T}\cdot\frac{1}{x} = C,$$

where x is defined above. This correction is, however, too empirical, and any attempt to modify Trouton's rule must take into account some function of α for both the liquid and gaseous state.

The rule of Eötvös may be treated in a similar manner. Thus the "normal" substances give a value for the constant $A = -2{\cdot}11$. If, however, we allow for association, we have

$$\frac{d\,.\,\gamma(Mv\,.\,x)^{2/3}}{dT} = A.$$

Substituting a mean value of $\alpha = {\cdot}80$ for the "normal" substances at the boiling-point, we find for the ideal associated state:

$$\frac{d\,.\,\gamma(Mv)^{2/3}}{dT} = -2{\cdot}44.$$

If we select water as typical of the associated substances, we find from the rule of Eötvös that at the boiling-point $x = 1{\cdot}7$ approximately. Using the value $A = 2{\cdot}44$, we find $x = 2{\cdot}1$ approximately, whereas the value of x deduced from the law of corresponding states is about 2·3. This assumes that x does not vary appreciably over the range used in

---

* *Ann. Chem. Phys.* xiii. p. 289 (1898).

calculating the constant of the expression, but, as shown in the tables above, this assumption is true over a range of about 10–20° C.

The application of the equation of state to the calculation of the degree of association of the "abnormal" substances must be deferred until the variation of the constants *a* and *b* of van der Waals' equation, with the degree of association, has been further investigated and placed on a more exact basis.

The author is indebted to Mr. J. B. P. Harrison, F.I.C., and Mr. A. L. Bloomfield, B.A., B.Sc., of these laboratories, for valuable criticisms and suggestions.

The Research Laboratories,
A. Boake, Roberts & Co. Ltd.,
Stratford, E. 15.

XXXIII. *Phase-effect and the Localization of Sound: an Examination of the Myers-Wilson Hypothesis.* By H. Banister, *B.Sc. (Lond.), Ph.D. (Cantab.), St. John's College, Cambridge* [*].

I. Introduction .... para. 1
II. The Myers-Wilson Hypothesis .... paras. 2, 3
III. Purpose of the Paper .... para. 4
IV. An Examination of the Assumptions on which the Myers-Wilson Hypothesis is based .... paras. 5–24
  (*a*) The three fundamental assumptions .... para. 5
  (*b*) The first assumption .... paras. 6–8
  (*c*) The second assumption .... paras. 9–12
  (*d*) The third assumption .... paras. 13–16
  (*e*) Sensitivity to binaural differences of intensity produced by cross conduction .... paras. 17–23
  (*f*) Conclusions regarding the validity of the assumptions.. para. 24
V. Mathematical Statement of the Myers-Wilson Hypothesis .... paras. 25–33
VI. Calculation of the Minimum Value of μ from Experimental Data .... paras. 34–46

---

[*] Communicated by the Author. This research was carried out in the Psychological Laboratory, Cambridge, with the aid of a grant from the Medical Research Council.

VII. Change in the Total Intensity of a Sound with Variations in the Relative Phases at the Ears.. paras. 47–80
  (*a*) Changes to be expected ...... paras. 47–51
  (*b*) Changes observed by previous experimenters .... paras. 52–59
  (*c*) Disadvantages of the "Binaural Beat" method of investigation .... paras. 60–61
  (*d*) Necessity of further investigation .... para. 62
  (*e*) Experimental determination of the change in intensity .... paras. 63–80
    i. Apparatus .... para. 63
    ii. Experimental Technique .... paras. 64–66
    iii. Reports of Observers .... paras. 67–79
    iv. Conclusion .... para. 80
VIII. Summary of the Results .... paras. 81–92
XI. Conclusion .... para. 93
Appendix.

I. Introduction.

1. ALTHOUGH, as I have pointed out in a previous paper *, Myers and Wilson were not the first to suggest that the "phase-effect" might be due to binaural differences of intensity brought about by bone conduction across the head, yet, since their statement of the hypothesis covers practically the whole field, and since the hypothesis is most generally, at least in English-speaking countries, associated with their names, it seemed appropriate that their account should form the basis of this inquiry.

II. The Myers-Wilson Hypothesis.

2. Myers and Wilson found that one sound was heard when the ears were stimulated separately and simultaneously by similar sound-waves of a given frequency; and that the localization of this sound depended on the relative phases of the vibrations at the ears.

3. They considered it very hard to believe that the phase differences were appreciated directly †, and suggested that the localization was actually based on subjective differences of intensity. They further showed that these differences of intensity might be objective to the inner ear, if certain assumptions were made.

---

* Phil. Mag. July 1926, p. 144.

† Brit. Journ. Psych. ii. p. 378 (1908).

III. PURPOSE OF THE PAPER.

4. In this paper I propose to examine their hypothesis. First, I shall discuss the assumptions on which the hypothesis is based, and then I shall consider deductions from the hypothesis which can be tested experimentally.

IV. AN EXAMINATION OF THE ASSUMPTIONS ON WHICH THE MYERS-WILSON HYPOTHESIS IS BASED.

(a) *The three fundamental assumptions.*

5. Myers and Wilson base their hypothesis on the three following assumptions *:—

(*a*) The sound entering one ear is transmitted through he bones of the head to the internal ear on the opposite side.

(*b*) The retardation in phase, due to this ear to ear conduction, is small.

(*c*) The two (direct and transmitted) sets of waves, at their meeting in one or other ear, arrive from opposite directions.

(b) *The first assumption.*

6. I have, in a previous paper(1) considered the evidence for the assumption that sound may be transmitted through the head, and it is therefore not necessary to enlarge on it here.

7. The conclusions reached were that there is no trustworthy evidence that aerial sound-waves, of normal intensity, exciting one ear, can be transmitted through the head to the other ear. The only direct evidence for bone conduction was obtained twenty-five years ago with dead heads(2). More recent experiments(3) have produced negative results, showing that the amount of sound energy which could enter the head was too small to be appreciated. Indirect experiments(4), (5), (1) are against the assumption. If there were transmission of sound through the head, it would still remain to be shown that the transmission was due to bone conduction. It might, with perhaps more plausibility, be set down to transmission through the sinuses of the head.

---

* Brit. Journ. Psych. ii. p. 378 (1908).

(1) Phil. Mag. July 1926, p. 144.

(2) Mader, *Sitzungsber. d. Kais. Akad. d. Wissens. Wien*, cix. pp. 37–75 (1900).

(3) Nikiforowsky, *Zeit. f. Sinnes Physiol.* xlvi. pp. 179–197 (1912).

(4) Cross & Godwin, Amer. Acad. Arts & Sci. n. s. xix. pp. 1–12 (1891).

(5) Peterson, Psych. Rev. xxiii. pp. 333–351 (1916).

8. So, though there is ample evidence that, *if* sound vibrations are set up in the bone of the head, they are conducted to the ears, there is no evidence, at present, to substantiate Myers and Wilson's assumption * that

> "it is impossible to stimulate the end organs of one ear without at the same time stimulating those of the other ear by bone conduction."

(c) *The second assumption.*

9. The second assumption (that the retardation in phase, due to this ear to ear conduction, is small) may be accepted if the first assumption (that there is ear to ear "bone conduction") is granted, for the velocity of the transmission of sound is very much greater in bone than in air.

10. If, however, there is transmission through the head, and if the transmission is through the sinuses and cavities of the head, the retardation of phase would very possibly be large, for the velocity of transmission through narrow tubes is much slower than in the open air.

11. But whether the retardation is large or small, the hypothesis is not substantially affected. If there is transmission through the head from one ear to the other, and if the rate of transmission through the head is different from that in the open air, the hypothesis in general holds. If the rate of transmission through the air is such that the phase retardation is between π and 2π, no change of sign, which is the essence of the third assumption, need be postulated; if the phase retardation due to the transmission through the head is less than π, the change of sign is necessary. I shall demonstrate the truth of this later (para. 30).

12. At the same time, as Rayleigh pointed out in 1909 †, there will be no retardation

> "if we are to suppose that the framework of the skull is thrown into vibration by sounds which enter by either ear"

unless we appeal to "viscous effects," when it "becomes a question whether the propagation across the head .... would suffice" to produce the effects observed.

(d) *The third assumption.*

13. The third assumption—that the direct and transmitted sets of waves, at their meeting, arrive from opposite

---

* Brit. Journ. Psych. ii. p. 380 (1908).

† Proc. Roy. Soc. lxxxiii. A, pp. 61-64 (1909); Scientific Papers, v. p. 524.

directions—is more difficult to accept, or to criticize, because the manner in which the vibrations are supposed to be set up in the bone at one side, and finally handed on to the end organs at the other side, is not stated. The assumption is, admittedly [*], made to suit the facts; but its validity is strongly stated [†]. No physiologist

> "will maintain that the vibrations which are thus conducted, say, from the left ear across the head, reach the end organs of the right ear by passing to the temporal, parietal, and occipital bones, which cover the right side of the skull, and that they then turn in towards the right inner ear by way presumably of the drum and ossicles, now accompanying the vibrations which travel to the right ear directly. There can be little doubt that the direct route is the only one which it is worth while to consider, the vibrations passing from one ear at once to the petrous portion of the opposite temporal bone in which the auditory end organs of that side are lodged."

14. Now, Foster [‡] states as follows:—

> "That the vibrations which thus [by bone conduction from a fork held between the teeth] reach the internal ear are, for the most part, at least, conducted through the tympanum, and not brought to bear on the perilymph directly through the bony walls of the labyrinth, is not only indicated by the effect just mentioned of closing the meatus, for this could have no influence on the labyrinth itself, but may be also proved by experiment. If a style be attached to a stapes laid bare in the skull, the vibrations of a tuning-fork brought into contact with the skull will lead to corresponding movements of the style."

15. It will thus be seen that one physiologist considered that sounds heard by bone conduction were communicated to the ear *viâ* the tympanic membrane, while later physiologists, *e.g.* Bezold and Liebenmann [§], held the same view. If the vibrations are communicated by the direct route, how are they to be supposed to act on the end organ? The mechanism of the bone conduction has not been outlined by Myers and Wilson with the fullness which is necessary for

---

[*] Proc. Roy. Soc. lxxx. A, p. 265 (1908).
[†] Brit. Journ. Psych. ii. p. 383 (1908).
[‡] 'Text-Book of Physiology,' 1891, p. 1332.
[§] 'Text-Book of Otology,' 1908.

any close criticism. One criticism was raised by Rayleigh[*], who pointed out in 1909 that the assumption, that two vibrations arriving at the inner ear from opposite directions co-operate if the phases are opposite and tend to neutralize one another if the phases are the same, is

> "justified if the effect depends upon the velocity of vibration, as when aerial waves impinge from opposite directions upon a sensitive flame. But if the question were the effect upon a resonator of the kind employed by Helmholtz, the direction of travel is indifferent, and co-operation, in all cases, required that the phases be the same."

16. The change of phase was, it would appear, introduced because the vehicle of the transmission through the head was supposed to be bone conduction. If the retardation of the transmitted wave is small—less than π—this change of phase is necessary, otherwise the result of assuming transmission would make the sound loudest at the ear which lags in phase. If, however, the retardation is between π and 2π, no change of phase is necessary. For a complete examination of the hypothesis we should consider the more generalized case, assuming that there is transmission through the head, and taking account of the two alternatives, when the retardation due to the transmission through the head is greater or less than π.

(e) *Sensitivity to binaural differences of intensity produced by cross conduction.*

17. Myers and Wilson appear to consider that the binaural differences of intensity produced by the cross-conducted sounds are small, for they quote two experiments[†] to show that we are "extraordinarily sensitive" to such differences of intensity.

18. The first experiment is the well-known one due to Weber, which they describe as follows:—

> "If a vibrating tuning-fork be placed on the vertex of the skull, its tone will be localized somewhere midway between the two ears. But if a finger be introduced into one auditory meatus, the apparent position of the tone is at once changed. It is localized on the same side as the auditory meatus into which the finger has been introduced."

---

[*] Proc. Roy. Soc. lxxxiii. A, p. 524 (1909).

[†] Brit. Journ. Psych. ii. p. 381 (1908).

19. The experiment does not, in my opinion, prove any extraordinary sensitivity. The physical effect of closing the meatus is at present very conjectural; while the psychological effect has not, so far as I am aware, been studied at all. But, ignoring any psychological factors, and confining our attention to the physical, I do not see how the effect could be a small one or one requiring any *extraordinary* sensitivity. If closing the meatus reflects the whole of the sound-waves back, the result would be stationary vibrations with twice the primary amplitude—*i. e.*, the intensity at that ear would be increased four times. If, owing to incomplete reflexion or other causes, the increase in intensity were as low as 50 per cent. instead of 400 per cent., it would be a matter for surprise if the increase were not recognizable. We have no quantitative results to argue on, but, *à priori*, one would be inclined to consider it extraordinary if the binaural difference of intensity, produced when the Weber experiment is performed, were not appreciable, if one of the chief effects of closing the meatus is to reflect the waves back again, and to set up stationary vibrations in the ear.

20. If, on the other hand, the physical effect of closing the ear is to make the meatus and its covering into a resonator, the binaural difference of intensity would again, in all probability, be considerable. While, if the tuning-fork sets the whole bony framework of the skull into vibration, as shown diagrammatically in fig. 1 by the whole and the dotted lines, then closing one meatus would perhaps, as suggested by Dr. Hartridge (personal communication), be equivalent to introducing another sound-producing apparatus; for, the tympanum being now prevented from moving with the bones of the head, the ossicles in contact with it are set into vibration relatively to the cochlea with

Fig. 1.

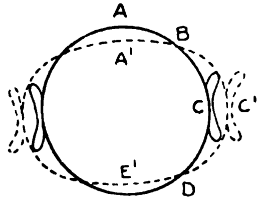
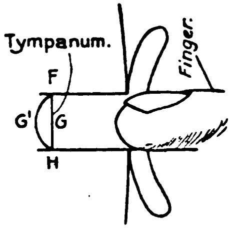


Diagram of pcssible mode of vibration of the skul.
A, B, C, D, E. One position.
A', B, C', D, E'. Another position.

a frequency equal to that with which the bones of the head are vibrating. This would obviously cause a large increase in the sound at that side (fig. 2).

Fig. 2.



As the bone at C (fig. 1) moves to C′, the air imprisoned by the finger forces the tympanum from the position F, G, H to F, G′, H.

21. So, however the physical effect may operate, we would expect the results of the Weber experiment to be what they are, without it being necessary to assume any great sensitivity on the part of the aural apparatus.

22. I have been unsuccessful in my attempt to repeat the second experiment, Schafer's modification of the Weber experiment, which Myers and Wilson thus describe:—

> "A fork, fixed at some distance from one side of the observer is very gently struck. The observer listens and notes when the dying tone has become quite inaudible. He then inserts an appropriately attuned resonator into the ear which is nearest the fork; whereupon, of course, the tone is at once softly heard again on that side, as if it came from the resonator. If the meatus of that more distant ear be now closed, the tone becomes at once stronger and its localization approaches the median plane."

23. A change is evident in the phenomenal experience when the finger is inserted in the ear; but I am unable to discriminate between this change and the change to be observed when the meatus is closed without the resonator being at the other ear. But, if there is bone conduction, which might perhaps be set up by the vibrating resonator inserted in the ear, then closing the other ear would probably, as in Weber's experiment, produce an appreciable increase in the intensity of the sound at that ear, and, in the absence of quantitative measurements, it would be improper to deduce that the ears are extraordinarily sensitive to small binaural differences of intensity caused by bone conduction; while

to assume that any phenomenal change that may occur is due to an intensity difference does not appear to be warranted.

Conclusions regarding the validity of the assumptions.

24. The result of this examination of the assumptions on which Myers and Wilson base their hypothesis may be briefly summarized as follows :—

(*a*) There is no evidence at present for the assumption that it is impossible to stimulate the end organs of one ear without at the same time stimulating those of the other ear, either by bone conduction or otherwise.

(*b*) Should there be transmission through the head there may be phase retardation.

(*c*) 1. If this phase retardation is between 0° and π, the waves arriving at one internal ear directly through the meatus must be considered as arriving "from opposite directions."

2. If the phase retardation is between π and 2π, it is not necessary to consider that the two sets of waves arrive "from opposite directions."

(*d*) There is no ground for assuming that the ears are exceptionally sensitive to binaural differences of intensity produced by bone conduction.

V. MATHEMATICAL STATEMENT OF THE MYERS-WILSON HYPOTHESIS.

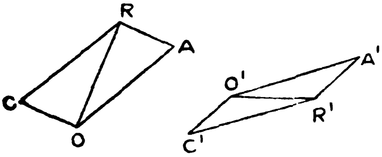
25. Now let us consider the argument of the Myers-Wilson hypothesis. It is as follows :—

Let OA (fig. 3) represent the physical vibration acting on the ear O, at any given instant, in amplitude and phase, and let O′A′ similarly represent the vibration acting on the ear O′ at the same instant. Then OC ($=\mu \times$ O′A′) will represent the vibration at O at that instant, due to bone conduction from O′, in amplitude and phase, where μ is a constant for the sound, and lies somewhere between the limits 0 and 1. The direction of OC will be determined by the fact that the sound takes a finite time to travel from O′ to O, so that the vibration will be later in phase than that at O′ by an amount which is less than π; and since the sound is travelling to the ear from the inside, its phase must be reversed. OR will then represent the resultant vibration at O in amplitude and phase. In the same way O′R′ will represent the resultant vibration at O′ in amplitude and phase. It is evident that, if OA leads in phase by an amount less than π, OR will be greater than O′R′; that is, the sound in the ear O will be louder than that in O′. In consequence of this resulting difference of intensity the sound will be localized on the side O.

26. The theory might with advantage have been stated more fully, for, as Rayleigh[*] has pointed out, if there is bone conduction the sounds must travel from O to O′, and back to O, and so on till they peter out. Put more generally then, we might say :—

Let OA (fig. 3) represent at any given instant the resultant effect of all the vibrations, due to the sounds which have entered the ear O from the outside, when the stationary condition has been reached at the ear O in amplitude and phase. This will evidently be proportional to the amplitude of the vibration of the external force (P). It will be the sum of the effect of P and of all the previous waves which have travelled from O to O′ and back to O, and which arrive at O at the same instant. There will also be acting on O a force, due to the external force (P′), acting on the ear O′. This force will be the resultant of all the waves which have traversed the various paths from O′ to O an odd number of times. It may be represented, in amplitude and phase, taking account of the assumed reversal of phase, by the line OC.

Fig. 3.



27. Assuming that the effective force of P on the ear O bears the same relation to the external force P, that the effective force of P′ on the ear O′ bears to the external force P′, and that OC$=\mu\times$(the effective force of P′ on O′), and O′C′$=\mu\times$(the effective force of P on O), where μ is a constant; it follows (1) that the difference of phase between OA and OA″ is equal to the difference of phase between P and P′; and (2) that the retardation of the phases of the vibrations received at either ear after traversing the skull an odd number of times will be later than the phases of OA and O′A′ by equal amounts. We may also, in view of the

---

[*] Proc. Roy. Soc. lxxxiii. A, pp. 61–64 (1909).

assumed proportionality between the external forces and the *effective* forces, neglect this constant of proportionality and consider P and P′ as the effective forces at the ears.

28. If, now, P is in advance of P′, the phase-difference being ϕ°, and if θ° is the amount by which the vibrations μP and $\mu P'$ are behind the vibrations P and P′ respectively, the resulting intensity at O is

$$P^2+\mu^2P'^2-2\mu\,.\,PP'\cos(\phi+\theta),\quad .\quad .\quad .\qquad (1)$$

and the resulting intensity at O′ is

$$P'^2+\mu^2P^2-2\mu\,.\,PP'\cos(\phi-\theta).\quad .\quad .\quad .\qquad (2)$$

If $P=P'$, we then have

$$I_0=P^2(1+\mu^2)-2\mu P^2\cos(\phi+\theta),\quad .\quad .\quad .\quad .\quad .\qquad (3)$$

$$=P^2[(1+\mu^2)-2\mu(\cos\phi\cos\theta-\sin\phi\sin\theta)],\quad .\qquad (4)$$

$$I_0'=P^2[(1+\mu^2)-2\mu(\cos\phi\cos\theta+\sin\phi\sin\theta)].\quad .\qquad (5)$$

Subtracting (5) from (4), we have

$$I_0-I_0'=4\mu\,.\,P^2\,.\,\sin\phi\,.\,\sin\theta,\quad .\quad .\quad .\quad .\qquad (6)$$

which is Myers and Wilson's value for the intensity differences at the ears, the perception (or, it may be, the unconscious sensing) of which is at the basis of our judgment of direction.

29. This difference of intensity vanishes for $\theta=0^\circ$ or π. It is greatest when $\theta=\pi/2$, so we see that, assuming transmission of sound through the head, the intensity at the ear leading in phase will always be greater than the intensity at the ear which lags in phase, provided the cross-conducted wave suffers a retardation of between 0^c and π, or of $(n\ 2\pi)+\theta$, where θ is between 0° and π, and assuming a phase reversal.

30. If the retardation of the transmitted wave is greater than π but less than 2π, *i. e.* it is equal to $(\pi+\theta)$, it is evident that the same result is obtained for the difference of intensities at the ears, without assuming that the "two (direct and transmitted) sets of waves, at their meeting in one or other ear, arrive from opposite directions"; that is, there is no necessity for the change of sign.

31. In this case, if θ is the whole retardation, the intensities (1) and (2) become

$$P^2+\mu P'^2+2\mu P\,.\,P'\cos(\phi+\theta),$$

and $$P'^2+\mu P^2+2\mu PP'\cos(\phi-\theta).$$

32. The difference of intensity given by (6) is greatest, for

any given value of θ, when $\phi=\pi/2$. The value then is

$$4 \,.\, \mu \,.\, P^2 \,.\, \sin\theta. \qquad (9)$$

33. The greatest possible value of this will result when $\theta=\pi/2$. It will then be

$$4 \,.\, \mu \,.\, P^2. \qquad (10)$$

VI. CALCULATION OF MINIMUM VALUE OF μ FROM EXPERIMENTAL DATA.

34. Let us now consider the case where there is a difference of physical intensity at the ears, but no phase-difference between the vibrations.

35. If P and P′ are the incoming external stimuli, the resultant intensity at the one ear is evidently, from para. 28 (1),

$$P^2+\mu^2P'^2-2\mu P \,.\, P'\cos\theta, \qquad (11)$$

and the intensity at the other is, from (2),

$$P'^2+\mu^2P^2-2\mu P \,.\, P'\cos\theta. \qquad (12)$$

The ratio of these intensities is

$$\frac{P^2+\mu^2P'^2-2\mu P \,.\, P'\cos\theta}{P'^2-\mu^2P^2-2\mu P \,.\, P'\cos\theta}. \qquad (13)$$

36. Now, if this ratio of objective intensities produces the same angular localization with reference to the median plane as the ratio of the subjective intensities when there is a difference of phase between the external vibrations, these vibrations being equal in amplitude, then these two intensity ratios can be equated, if we assume that the ear appreciates the two intensity ratios in the same way.

37. This latter ratio, from equations (3) and (5) (para. 28) is

$$\frac{P^2(1+\mu^2)-2\mu P^2\cos(\phi+\theta)}{P^2(1+\mu^2)-2\mu P^2\cos(\phi-\theta)}. \qquad (14)$$

38. In a previous experiment * I found that the minimum ratio of the intensities of the external vibrations which produced the same angular localization as a phase-difference of $\pi/2$ was 2·50.

39. Substituting these values in (13) and (14) and equating, we get:

$$\frac{2{\cdot}50+\mu^2-2\mu\times1{\cdot}6\times\cos\theta}{1+\mu^2\times2{\cdot}50-2\mu\times1{\cdot}6\times\cos\theta}$$
$$=\frac{1+\mu^2+2\mu\sin\theta}{1+\mu^2-2\mu\sin\theta}. \qquad (15)$$

---

* Brit. Journ. Psych. xvi. p. 265 (1926).

If θ is greater than π, and the cross-conducted wave is not supposed to undergo a change of phase of π, the equations are:

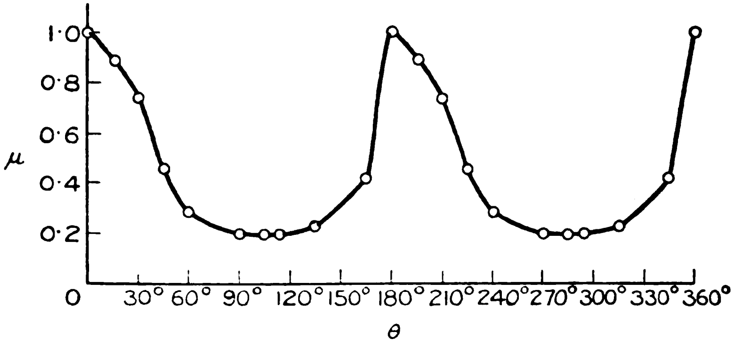
$$\frac{2\cdot50+\mu^2+2\mu\times1\cdot6\times\cos\theta}{1+2\cdot50\mu^2+2\mu\times1\cdot6\times\cos\theta}=\frac{1+\mu^2-2\mu\sin\theta}{1+\mu^2+2\mu\sin\theta}\quad . \quad . \quad . \qquad (16)$$

40. The variation of μ *, as θ increases from 0° to 360°, is shown in Table I. and fig. 4.

TABLE I.

θ.			μ.
0°	or	180°	1·0
15	or	195	0·89
30	or	210	0·77
.45	or	225	0·46
60	or	240	0·29
90	or	270	0·20
105	or	285	0·20
115	or	295	0·20
135	or	315	0·23
165	or	345	0·42

Fig. 4.



The values of μ and θ which satisfy the equations (15) and (16).

μ = proportion of sound which is transmitted through the head from one ear to the other.

θ = phase-retardation of the transmitted wave.

---

[*] The method of obtaining the value of μ for any given value of θ is given in the Appendix.

41. The graph shows very clearly that, if the phase-effect is a subjective differential intensity effect, which is produced by the transmission of the sound through the head from one ear to the other, and if this difference of intensity is proportionally the same as that which is required objectively to produce an equal angular displacement of the sound from the median plane when there is no difference of phase between the external vibrations, the proportion of the sound which is transmitted through the head will have a value between ·20 and 1·0, depending on the retardation in phase brought about by the transmission.

42. If the retardation of phase is small, as Myers and Wilson assume, *e. g.* 15°, then $\mu = 0{\cdot}89$. This would mean that, if the right ear were stimulated directly, the amplitude of the vibration transmitted to the left ear would be 89 per cent. of that at the right ear.

43. Under the most favourable conditions, when the phase retardation is about 90° to 120° (or 270° to 300°), the amount of sound conducted through the head is about one-fifth.

44. Now this is *the minimum* value for μ. It is obtained by assuming the most favourable value for the phase-retardation, and using the smallest value (2·50 : 1) for the intensity ratio which would produce the same angular localization as a phase difference of $\pi/2$. For the intensity ratio of 11·8 : 1, the maximum for my observers [*], the minimum value of μ, with the most favourable phase-retardation, is ·35. For Stewart's [†] figure of 33 : 1 for the intensity ratio the minimum value of μ is greater still.

45. It seems very improbable that, if μ has even the smallest value (0·20), my previous experiments [‡], when I was searching for evidence for the direct transmission of sound through the head, could have produced only negative results. Also, if there is transmission of this magnitude, individuals, deaf in one ear, should have little difficulty in hearing with the normal ear sounds, led to the deaf ear: but it is stated [§] that such individuals cannot hear unless the intensity of the sound is raised to about 10,000 times that required for audition if the sound is led to the good ear directly.

46. This investigation would, therefore, seem to indicate that the Wilson-Myers explanation of the phase effect is not correct.

---

[*] Brit. Journ. Psych. xvi. p. 286 (1926).

[†] Phys. Rev. 2nd ser. xv. p. 425 (1920).

[‡] Phil. Mag. July 1926, p. 144.

[§] Wegel & Lane, Phys. Rev. xxiii. pp. 266-285 (1924).

VII. CHANGE IN THE TOTAL INTENSITY OF A SOUND WITH VARIATIONS IN RELATIVE PHASES AT THE EARS.

(a) *Changes to be expected.*

47. If the ears are being stimulated with sounds of equal objective amplitude, but differing in phase, the effective intensities of the sounds at the ears, assuming transmission of the sound through the head from one ear to the other, are given by (4) and (5), para. 28. These are:

$$P^2\left[(1+\mu^2)-2\mu\,(\cos\phi\cos\theta-\sin\phi\sin\theta)\right]$$

and $$P^2\left[(1+\mu^2)-2\mu\,(\cos\phi\cos\theta+\sin\phi\sin\theta)\right].$$

The total intensity of the sound is therefore

$$2\,P^2\left[(1+\mu^2)-2\mu\cos\phi\,.\,\cos\theta\right]. \quad . \quad . \quad (17)$$

48. For any given individual and a tone of given pitch, μ and θ will be constant. We therefore have that the total intensity will vary as the relative phases of the external vibrations vary. It will be a maximum when

$$2\mu\cos\phi\cos\theta \text{ is a minimum ;} \quad . \quad . \quad . \quad . \quad (18)$$

and a minimum when

$$2\mu\cos\phi\cos\theta \text{ is a maximum.} \quad . \quad . \quad . \quad . \quad (19)$$

Since μ and θ are constant,

$2\mu\cos\phi\cos\theta$ will be a minimum when

$\cos\phi$ is a minimum.

The smallest value of $\cos\phi$ is -1 when $\phi=180°$;

The greatest value of $\cos\phi$ is $+1$ when $\phi=0°$.

49. So we see that the total intensity of the sound is, according to the Myers-Wilson hypothesis, a maximum when the difference between the phases of the external vibrations is 180° : it is a minimum when the vibrations are in phase.

50. This same relation holds, if the phase-retardation of the transmitted sound (θ) is between π and 2π, if no change of phase is postulated.

51. For other cases (θ less than π, and no change of phase ; or θ between π and 2π and a change of phase) the total intensity will be a maximum when the external vibrations are in phase and a minimum when their phases differ by π. But if the maxima and minima vary in this way, the experiment furnishes evidence which is a direct contradiction of the Myers-Wilson hypothesis.

(b) *Changes observed by previous experimenters.*

52. A certain amount of work has already been done on the variation in the intensity of binaurally heard sounds with change in the relative phases at the ears; but, as I shall show, the results do not agree.

53. The variation of relative phase has usually been obtained by leading sound waves from two slightly mistuned forks, or other sources of sound, to the ears separately. Binaural beats then occur, and the various phenomena connected with these beats can be observed as the relative phases at the ears vary from 0° to π and back again to 0°.

54. *Thompson*, 1877.—Thompson [*] was one of the first to remark on variations of intensity so observed. With slow beats, less than two per second, he says:—

> "There was no very decided weakening of the intensity of the sound comparable to the 'silences' ordinarily observed between the 'beats,' the two tones seeming to be going on, but with a difference hardly definable in precise terms. When complete difference of phase was momentarily attained, there seemed to be a slight increase in the intensity of the sound, and the octave note (which, it will be remembered, is not amongst the upper partials of the fork) was faintly heard."

So, though he did not find any "very decided weakening," there still "seemed to be a slight increase in the intensity of sound" when there was a difference of phase of π. A result which supports the Myers-Wilson hypothesis.

55. *Rostosky*, 1902.—Rostosky [†] noted intensity variations in binaural beats in 1902; but he found the maximum intensity was when the sounds were in phase, and that, when the beats were slower than one in two to five seconds, other maxima appeared just before and just after the opposition of phase. These observations are antagonistic to the Myers-Wilson hypothesis. The maxima and minima are reversed, while secondary maxima occur!

56. *More & Fry*, 1907.—Five years later More and Fry [‡] paid attention

> "to the question whether difference in phase produced a change in the intensity of the combined tones. . . . . Not one of [14] observers could detect any alteration in the loudness of the sounds when the relative phases were varied."

---

[*] Phil. Mag. (5) iv. pp. 274–276 (1877).

[†] Philos. Stud. xix. pp. 557–598 (1902).

[‡] Phil. Mag. [6] xiii. pp. 452–457 (1907).

These experimenters, I would remark, used apparatus similar to that employed later by Myers and Wilson. They obtained their difference of phase by varying the lengths of the pathways by which the sounds were led from a single source to the ears. They did not study the phenomena of binaural beats.

57. *Stewart*, 1917.—In 1917 Stewart* published the result of an investigation he made into the maxima and minima to be observed with binaural beats, with special reference to Rostosky's experiments. He remarks*:—

> "One [maximum intensity] occurred at 0° difference of phase, one at $180°-\delta$ and one at $180°+\delta$, δ being less than 45°. The earlier of the additional maxima at $180°-\delta$ phase difference coincided with the localization in the ear near the higher frequency, and the latter with the localization in the other ear. . . . . The significant fact is that the 0° maximum was always present, whereas the secondary ones required a beat period exceeding at least a second in order to become clearly evident. . . . . The localization in the ears as described seemed to depend upon the perception of the secondary maxima."

We see, then, that his observations agree with those of Rostosky, but that they disagree with the Myers-Wilson hypothesis.

58. *Banister*, 1925.—My own results, previous to the investigation about to be described—side remarks made by observers in other experiments—had shown equal diversity. Only once† had an observer specially attended to intensity differences. I was then determining the binaural intensity ratio which would produce the same angular localization of a tone as a phase-difference of $\pi/2$. This observer correctly picked out the "phase-effect," differentiating it from the intensity effect, because with the former he could not appreciate any change in the loudness of the sound.

59. We see, then, that there is a difference of opinion, first of all whether a change in the relative phases of the vibrations at the ears causes any change in the loudness of the sound or not; secondly, whether the maximum, if there is one, is when the vibrations are "in phase" or when the phase-difference is 180°.

---

* Psych. Monogr. xxv. pp. 31-46 (1917-18); Phys. Rev. ix. pp. 502-528 (1917).

† Brit. Journ. Psych. xvi. p. 288 (1926).

(c) *Disadvantages of the "Binaural Beat" method of investigation.*

60. Now, though a study of variations in loudness due to phase changes is experimentally most easily made by listening to binaural beats, phenomenally such a method of investigation is fraught with difficulty. The sound is moving about from side to side all the time, and the way in which it moves is different for different people—some (*e. g.* Stewart) appear to hear the sound outside the head in front for a part of the cycle and inside the head for the rest; others hear the sound behind instead of in front; others only hear the sound inside the head; with some the sound travels in a horizontal plane; with others the same sound physically moves in a plane, making an angle of perhaps 60° with the horizontal. Again, with some observers the pitch of the sound varies with its position, while, more important still, the apparent distance of the sound varies from point to point. Another most important attribute, very distinct from loudness, but yet one which may easily be confused with loudness, is volume; and volume again varies with position, though what the relation between volume and phase difference at the ears is has not yet been settled. The observations so far available—*e. g.* Wilson and Myers [*], Peterson [†], Halverson [‡]—are not sufficient for any generalizations to be made. Now it is evident that one and all of these factors may enter into our judgment of "loudness"; so that it would seem desirable to eliminate them, as far as is possible, by using sounds which are not continually changing in position.

61. Another very serious objection to the binaural beat method of study is that no controls are possible, and the same error, should there be one, will creep in again and again, and may perhaps be accentuated by use.

(d) *Necessity of further investigation.*

62. It therefore seemed important that an investigation should be made into the variations in loudness produced by changing the relative phases of the vibrations of the sound waves at the ears, the amplitudes of the vibrations being kept constant.

---

[*] Brit. Journ. Psych. ii. p. 369 (1908).

[†] Phys. Rev. xxiii. pp. 333-351 (1916).

[‡] Psych. Monogr. xxxi. pp. 7-29 (1922); Amer. Journ. Psych. xxxiii. p. 179 (1922).

(e) *Experimental determination of the change in intensity.*

(i.) *Apparatus.*

63. The apparatus was that used in previous experiments *, and is shown diagrammatically in fig. 5.

Fig. 5.

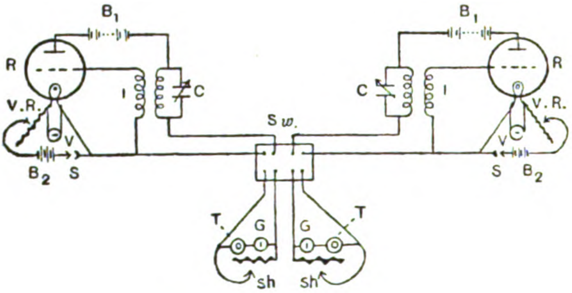


Diagram of Apparatus.

B_1. High-Potential Battery (54 volts.). B_2. Accumulator (6 volts). C. Variable Condenser. G. Milliammeter. I. Inductances. R. Valve. S. Switch. *sh.* Shunt. T. Telephone. V. Voltmeter. V.R. Variable Resistance. S*w.* 4-way Switch.

(ii.) *Experimental Technique.*

64. The observer, with head-phones on, sat in the sound-proof room; the experimenter in the annexe. Communication was, as before, by microphone from Observer to Experimenter and by speaking-tube from Experimenter to Observer. When ready, the observer said "Ready!", and the sounds, in phase, were switched on. The sound was then centred and switched off. After a short interval the sounds were switched on to verify that the sound was still in the median plane; if it were not, adjustments were made. This was repeated, if necessary, till the observer reported that the sound was in the centre. The current passing through the telephones was then noted. (This current is, as I have already shown †, proportional to the amplitude of vibration of the telephone diaphragm.) The experiment then began. The experimenter switched on the sounds. The observer listened,

---

* Brit. Journ. Psych xv. pp. 280–307 (1925); xvi. pp. 265-292; Phil. Mag. July 1926, p. 144.

† Brit. Journ. Psych. xvi. p. 281 (1926).

satisfied himself that he had the sound properly under observation, signalled to that effect by gently touching the microphone, and listened to see if he detected any change in loudness. The experimenter meanwhile made a change in phase of π, or a change of intensity—either increasing or decreasing the intensity—or else he made no change at all. The sounds were continued for about four seconds, and then switched off. The observer wrote down his observation on a specially prepared form, with separate columns for Louder, Equal, and Softer, and remarked on any matter of interest. The experimenter also noted down what change he had made, re-adjusted the apparatus to its initial condition, and waited for the "Ready!" from the observer, when the next observation was taken. Since the observer had to judge changes in loudness only, the sounds were not centred for each observation. Variations in the position of the sound were sometimes remarked on; but, though of interest, the observations made are too scattered to justify discussion here. The sound was centred before the first and the eleventh observations only—*i. e.*, when the telephones were first put on and when they were changed round. The sound used was an impure tone of about 220 d.v./sec.

65. Twenty observations were taken at each sitting, which usually lasted for about half-an-hour.

66. Four observers, two men and two women, took part in the experiment. Three of them, A, B, and F, had observed for me previously. The fourth, (G), a man, was new. The observers were not equally able to give me of their time, so the number of observations obtained from them is not constant.

(iii.) *Reports of Observers.*

67. The reports are summarized in Table II., which shows, for example, that the experimenter decreased the amplitude of the vibration at one ear to between 81 per cent. and 90 per cent. of its initial value eighteen times for observer A, who judged that the sound became louder three times, softer eleven times, while she detected no change in loudness four times. The experimenter made "no change," either of phase or of intensity, nineteen times for observer B, who reported that there was no change in loudness on twelve of these occasions, but that, on the other seven occasions, the sound appeared to become softer.

TABLE II.

Change made by Experimenter.	Initial amplitude of the vibration at one side																														No change.			Phase-change 0° to π.		
	decreased to between these percentage limits.												increased to between these percentage limits.																							
	0–70			71–80			81–90			91–100			101–110			111–120			121–130			131–140			141–150			151–								
Observer.	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S
A	–	1	4	2	2	7	3	4	11	–	1	1	1	1	1	7	5	–	11	3	–	–	–	–	1	–	–	2	–	–	5	21	4	7	36	3
B	–	–	3	–	2	1	4	1	3	–	1	–	–	–	–	8	3	–	2	1	–	2	1	–	–	–	–	–	–	–	7	12	–	12	9	1
F	–	1	1	–	–	2	1	4	3	–	1	1	–	2	1	4	2	–	4	–	–	–	–	–	1	–	–	1	–	–	1	10	2	10	11	3
G	1	–	1	1	8	1	8	7	–	–	–	–	2	–	–	5	3	–	9	–	–	1	–	–	1	–	–	2	–	–	13	17	–	24	9	–

Table showing the number of times each observer judged that the change made by the experimenter caused the total **sound to appear to grow louder (L), to grow softer (S), or to remain of constant loudness (E).**

68. It will be noticed that every observer reported an increase of loudness more often than a decrease when the relative phases at the ears were varied from 0° to π, and that two (B & G) showed a very marked tendency to judge that the sound had become louder. This is, *prima facie*, evidence for the Myers-Wilson hypothesis.

69. But let us examine the whole data more fully, beginning with F. F clearly differentiated the "No change." On three out of thirteen such observations he recorded changes of loudness—once an increase and twice a decrease. He, also, could discriminate and judge correctly when the amplitude of the vibration to one side was increased to 111 per cent. or more of the initial amplitude, or when it was decreased to 90 per cent or less. Out of twenty-four observations, when the phase was changed from 0° to π, he reported an increase in loudness ten times, "No change" eleven times, and a decrease three times. This observer had four sittings. At the first, his report for the phase-change was 5 louder ; 3 equal ; nil softer.
At the second, he reported 4 ,, ; 3 ,, ; 1 softer.
At the third, ,, nil ,, ; 1 ,, ; 2 ,,
At the fourth, ,, 1 ,, ; 4 ,, ; nil ,,

He made no introspective remarks of interest. But the fact that at his third and fourth sittings he reported one louder, five equal, and two softer would seem to point to the possibility of his having learned with practice to discriminate variations of loudness from variations in other ways.

70. (A) discriminated the "No change" fairly successfully, but for the phase-change reported more increases than decreases in loudness. She also could, obviously, tell when the amplitude of the vibration at one side was increased, or decreased, by 10 per cent.

71. A gave me eight sittings. Her reports, when the relative phases were changed from 0° to π, were :—

Louder.	Equal.	Softer.	Remarks by Observer.
2	4	0	x Equal or softer. * Equal or louder.
2	6	0	
2	5	1	
–	2	1x	
1*	4	1x	
–	5	–	
–	5	–	
–	5	–	
7	36	3	

72. We see that, after her first three sittings, she reported changes of loudness only three times out of twenty-four observations, and, on each of these three occasions (of which only one was a judgment of increase), she queried the change.

73. This observer's remarks are interesting. The first day she reported much difficulty in forming a judgment of loudness when listening to the phase-change, but none when the phase did not change. She ascribed this to the movement which occurred. Her remarks for the two occasions on which she reported an increase were "Large change in position—very muddling." "Very difficult because of change in position." But before the end she began to differentiate, and she remarked that what she at first thought was an increase in loudness was really some change or other in what she called "quality"—some change she found it difficult to describe. Thereafter this uncertainty gradually gave way to certainty that there was no variation in loudness, but some other change, due somehow or other to the change in the position of the sound, which change in position she later decided was a movement from one point in the median plane to some other point in the median plane. When the sound was at the second position in the median plane (phase-difference π), she described it as "a curiously exciting noise. It is very thrilling. It gives me the impression of going up and perhaps becoming clearer."

74. (A) therefore, if the first sittings are considered, as they reasonably may, to be preliminary practice sittings, definitely could not distinguish any change in the intensity of the sounds when the relative phases at the ears were changed from 0° to π, though she could discriminate a change in the amplitude of the vibration at one side of 10 per cent.—which is a change of not more than 10·5 per cent. in the total physical intensity of the sounds acting on her ears.

75. But (B) and (G) are different. They both, on the average, judged that the sounds had become louder when the relative phases were changed from 0° to π; and also they judged that the sound became louder even when no change whatever was made. (B) came only four times, whilst (G) came six times. Their judgments on each of these occasions were :—

Observer.	No change made.			Relative phases changed from 0° to π.		
	L	E	S	L	E	S
(B)	3	–	–	1	4	1
	3	4	–	2	1	–
	1	3	–	5	2	–
	–	5	–	4	2	–
	7	12	0	12	9	1
(G)	6	1	–	2	1	–
	2	2	–	5	–	–
	2	3	–	4	2	–
	1	4	–	4	2	–
	1	4	–	4	2	–
	1	3	–	5	2	–
	13	17	0	24	9	0

L = Louder. E = No change. S = Softer.

(G), it will be noticed, judged at his first sitting that the sound went louder six times out of the seven times no change was made; the next sitting he judged more correctly, and, though there was still a tendency to judge that the loudness was increased when no change was made in the intensity, he discriminated the "No change" observations with reasonable accuracy at his fourth and subsequent sittings. He, however, still continued, in no uncertain manner, to judge that there was an increase in loudness when the relative phases were varied from 0° to π. (B)'s results show a very similar tendency.

76. These two observers are also alike in another respect. They judge, as a reference to Table II. will show, that the sound *increased in loudness* when the *physical intensity decreased*, provided the decrease was not too great. It will be seen that, when the amplitude to one side was decreased from 81–90 per cent., (B)'s judgments for 8 observations were: 4 louder, 1 equal, and 3 softer; while (G) judged 15 observations to be 8 louder and 7 equal.

77. In spite of these peculiarities, it might be argued that the evidence of these two is in favour of the Myers-Wilson hypothesis. It is not a sufficient answer to state that the

observers were judging a change in some other attribute of situation as an increase of loudness. The obvious course was to try the same experiment again, but this time to vary the phases the opposite way, from π to 0°. Since the change from 0° to π produced an increase in loudness, a change from π to 0° should cause a decrease in loudness. Unfortunately, one observer left Cambridge temporarily, while the other become ill, so the experiment could not be performed till six weeks later, when observer (A) also gave me two more sittings. The observations then obtained when "No change" was made, and when the relative phases were varied from π to 0°, were:—

Observer.	No change made.			Relative phases changed from π–0.		
	L	E	S	L	E	S
B (2 sittings)	3	8	0	10	3	0
G (3 sittings)	5	9	1	10	10	0
A (2 sittings)	0	10	0	1	14	0

L = Louder. E = No change. S = Softer.

78. It will be seen that (A)'s report agrees with her previous ones. She reported a change of "some description," but not of loudness when the relative phases were changed from π to 0°; while (B) and (G) showed the same tendency to report an increase of loudness when "No change" was made, and, instead of the phase-change producing a *decrease* in intensity, an *increase* was reported. It therefore, I think, appears evident that, in judging the sound to have become louder, these two observers were not discriminating the loudness from the other factors in the situation.

79. It would seem that this is the true explanation of the observations of Thompson, Rostosky, and Stewart. In judging variations in loudness, they probably did not discriminate—their experimental method made it almost

impossible—between variations in loudness and variations in the other attributes of the sounds they used. Also their experiments lacked control, as I have pointed out in para. 61.

(iv.) *Conclusion.*

80. The conclusion to which this experiment forces us is, therefore, that, if tones of the same frequency are led separately to each ear, there is no appreciable difference in the loudness of the resulting sound whatever the relative phases of the vibrations may be, provided the amplitudes are kept constant; while there is evidence that a change of 10 per cent. in total intensity is discernible *.

VIII. SUMMARY OF THE RESULTS.

81. Let us now briefly summarize the results arrived at in this and other papers †, so far as they bear on the hypothesis that the "phase-effect" is to be explained as an "intensity effect" brought about by the transmission of sound energy from one ear to the other through the head.

82. (1) The evidence for the first assumption made by Myers and Wilson, that "the sound entering one ear is transmitted through the bones of the head to the opposite ear," has been examined †. It has been shown that the experimental evidence adduced in support of the assumption will not stand critical examination. The most refined experimental methods, so far used, have failed to demonstrate that there is any transmission of sounds of ordinary intensities from one ear to the other, either by bone conduction or by any other means, in the living head.

83. (2) The second assumption, "that the retardation in phase due to such internal conduction is small," may be accepted. Unless there is some phase-difference, the transmission of the sound could not produce any binaural intensity difference. At the same time the magnitude of this assumed phase-retardation is immaterial to the general argument.

84. (3) The third assumption, "that the two sets of waves thus received at each ear directly and by bone conduction, meet coming from opposite directions," was made to account for the facts. It is necessary to assume this change of phase if the phase-retardation (assumption 2) is small. If the phase-retardation is between π and 2π, this change of phase need

---

* This 10 per-cent. limen must not be considered as anything more than indicating that my observers could appreciate this variation in intensity with sounds of the loudness used. But it agrees with the value found by Knudson (Phys. Rev. xxi. pp. 84–102, 1923).

† Brit. Journ. Psych. xvi. p. 265 (1926). Phil. Mag. July 1926, p. 144.

not be assumed. There is a difference of opinion among physiologists as to the legitimacy of the assumption, but our knowledge of the whole mechanism of the transmission of sound through the head, if it takes place, is so nebulous that the assumption cannot profitably be criticized.

85. (4) Binaural difference tones cannot be heard, though binaural beats can. If the latter are due to interference at the end organs, due to transmission of the sound through the head, it is difficult to understand why binaural difference tones cannot be obtained [*].

86. (5) Assuming that the Myers-Wilson hypothesis is correct, and that the phase-effect is on analysis an intensity effect, experiments were performed [†] to determine what differences of objective physical intensity at the ears, when the vibrations were in phase, would produce the same angular localization of the sound as a phase-difference of $\pi/2$ when the intensities of the sounds remained equal.

87. Two methods were employed: (*a*) the "Method of Production," the relative intensities being varied till the sound appeared to occupy the same angular position, with reference to the median plane, as it occupied when the relative phases only were changed; and (*b*) the "Method of Presentation," the observer reporting whether a given binaural intensity-difference produced a greater, equal, or lesser angular localization of sound with reference to the median plane when compared with the deviation produced by the phase-difference.

88. The two methods show a remarkable agreement for individual observers; but there are great differences between the various observers. The least binaural ratio of intensity required to produce the same angular localization as was caused by a difference [‡] of phase of $\pi/2$ was 2·5 : 1; the greatest was 11·8 : 1.

89. (6) If a binaural ratio of intensity of 2·5 : 1 could result from the transmission of sound through the head, the minimum value for μ (the ratio of the subjective amplitudes of the vibrations at the ears when a sound is led to one ear) is ·20—the phase-retardation would then be about 90° to 120°. For a binaural intensity ratio of 11·80 : 1 the minimum value of μ is ·35.

90. It is incredible that such large proportional amounts of energy could be transmitted and escape detection. (This paper, paras. 34–46.)

---

[*] Phil. Mag. July 1926, p. 144.

[†] Brit. Journ. Psych. xvi. p. 265 (1926).

[‡] Brit. Journ. Psych. xvi. p. 286 (1926).

91. (7) If the "phase-effect" is due to transmission through the head, the total sound heard should vary in loudness as the relative phases of the vibrations at the ears vary. The total sound will, according to the Myers-Wilson statement of the hypothesis, be loudest when the vibrations differ in phase by π, and quietest when there is no difference in phase. (If the phase-retardation due to the transmission lies between π and 2π, the opposite effect will occur.) Carefully controlled experiments produced no evidence for this variation in loudness. At the same time, a difference of total intensity of 10 per cent. was easily appreciated. (This paper, paras. 47–80.)

92. (8) According to the Myers-Wilson hypothesis, the phenomenal effects of varying the bilateral intensities of the sounds at the two ears should be independent of the relative binaural phases. This is not borne out by experiment. The observed facts agree with the hypothesis that the phase-effect is not an intensity effect *.

IX. Conclusion.

93. We see, then, that the Myers-Wilson hypothesis has in no single instance been supported by experiment. The conclusion is that any hypothesis is wrong which seeks to explain the facts, of sound-localization by binaural phase-differences, on the assumption that there is transmission of sound from one ear to the other through the head, and that this transmission causes the actual intensity of the sound at the ear which leads in phase to be greater than the intensity at the ear which lags in phase.

Appendix.

Method for determining the graph for μ as a function of θ from equation (15), para. 39 :

$$\frac{2{\cdot}50+\mu^2-3{\cdot}2\mu\cos\theta}{1+2{\cdot}50\mu^2-3{\cdot}2\mu\cos\theta}=\frac{1+\mu^2+2\mu\sin\theta}{1+\mu^2-2\mu\sin\theta}.$$

Plot the curves $y_1=\dfrac{2{\cdot}50+\mu^2-3{\cdot}2\mu\cos\theta}{1+2{\cdot}50\mu^2-3{\cdot}2\mu\cos\theta}$

and $y_2=\dfrac{1+\mu^2-2\mu\sin\theta}{1+\mu^2-2\mu\sin\theta}$

between the limits $\mu=0$ and $\mu=1$, for various values of θ.

The point of intersection of the curves gives, evidently, the value of μ which satisfies equation (15) for the specific values of θ taken

---

* Brit. Journ. Psych. xvi. p. 265 (1926).

For example :

Let us find the value of μ if θ, the phase-retardation in passing through the head from one ear to the other, is 60°.

If $\theta = 60°$, $\sin\theta = \cdot 87$, $\cos\theta = \cdot 5$, so the equations for y_1 and y_2 may be written

$$y_1 = \frac{2\cdot 50 + \mu^2 - 1\cdot 6\mu}{1 + 2\cdot 50\mu^2 - 1\cdot 6\mu},$$

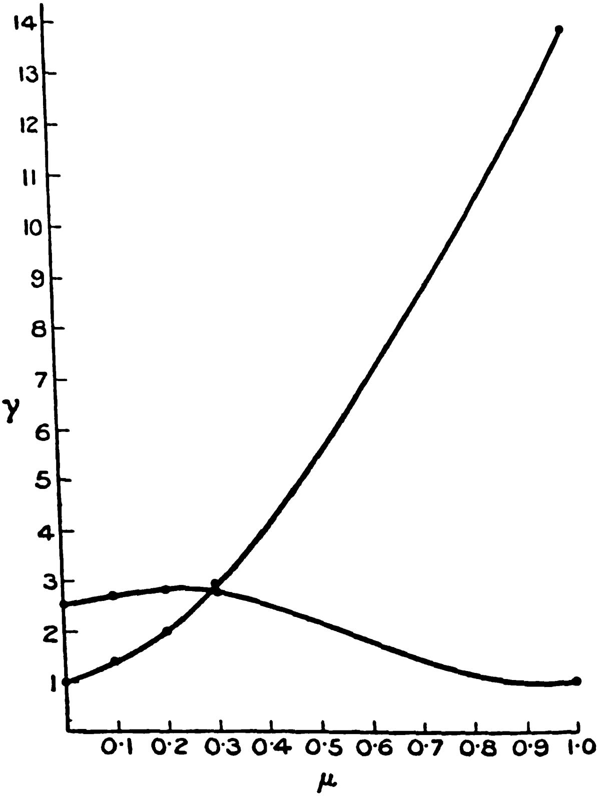
$$y_2 = \frac{1 + \mu^2 + 1\cdot 74\mu}{1 + \mu^2 - 1\cdot 74\mu}.$$

Evaluating y_1 and y_2 for various values of μ between 0 and 1, we get

μ.	y_1.	y_2.
0	2·50	1
.1	2·7	1·4
·2	2·85	2·0
·3	2·83	2·9
1·0	1	14·4

Plotting these values of y_1 and y_2, we obtain the curves of fig. 6.

Fig. 6.



From which we get, by inspection, the value of μ as 0·29 when $\theta = 60^\circ$.

In a similar way we find the following pairs of values, which on plotting give the curve of fig. 4, para. 40 :—

θ	0°	15°	30°	45°	60°	90°
μ	1	0·89	0·77	0·46	0·29	0·20

θ	105°	115°	135°	165°	180°
μ	0·20	0·20	0·23	0·42	1·0

XXXIV. *The Elasticity Coefficients and the Thermodynamic Integration Factor for the Solid State.* By A. Press, *Rockefeller Foundation Visiting Professor of Physics, Chulalongkorn University, Bangkok, Siam* *.

The Generalized Thermodynamic Equation of State.

THE work of Grüneisen and Ratnowsky, mentioned in the text of Andrews's article on "The Relation between Young's Modulus and the Temperature" (see Phil. Mag. October 1925, p. 667), led to the questioned conclusion "that $\frac{V\beta}{k_T}$ should be the same function of the corresponding temperature for all substances...." Here k_T is the isothermal compressibility, V the atomic volume, and β the coefficient of cubical expansion. The above formula, be it noted, was derived by Ratnowsky by applying the quantum theory to Grüneisen's work after the Debye manner. In checking up the above formula, it was found that the metals Fe, Ni, Zn; Ag, Sn; Au, Pt, Pb, for example, grouped together rather according to the same row of the periodic table than according to the same column, which result was quite unexpected. It will be shown herewith, however, on theoretical grounds that a density factor d should have occurred in the formula to justify the observed row grouping of the elements.

---

* Communicated by Prof. I. J. Schwatt, Ph.D.

It is also to be borne in mind that if at points far removed from the actual change of state the ratio $\frac{\beta}{k_T}$ can be made to conform to a modified Grüneisen-Ratnowsky type of formula, for a proper generalized understanding of all the thermodynamic factors to appear, one and the same covering expression for such ratio should obtain for the change of state itself. That is to say, the one general formula should lead to the expression $\frac{\beta}{k_T}=\frac{\lambda}{t}$, where λ is now the internal latent heat of the body. (See Edser, Fourth Report on Colloid Chemistry, Brit. Assoc. Adv. Sci. 1922.) It will be shown that the generalized thermodynamic treatment herewith satisfies the above two conditions. Indeed, it also leads to the further Grüneisen condition that the specific heat at sufficiently low temperatures is proportional to the thermal coefficient of expansion divided by the compressibility. In accordance with Debye, it is known that the compressibility should also vary little with the temperature.

The starting-point is therefore to be made with the energy equation

$$dQ=\frac{\partial U}{\partial t}\,.\,dt+\left(\frac{\partial U}{\partial v}+p\right)dv.$$

Instead, then, of employing the more usual integrating factor $\mu=1/t$, which, in fact, mathematically at least, limits the solution considerably, a more general type of integrating function

$$\mu=f(t,v)$$

will be taken with the understanding that the precise form of μ is to be deduced theoretically as a consequence of experimental fact. Thus applying the condition for a complete differential, we have that

$$p+\frac{\partial U}{\partial v}+\frac{\mu}{\frac{\partial \mu}{\partial t}}\cdot\frac{\partial p}{\partial t}=\frac{\partial U}{\partial t}\cdot\frac{\frac{\partial \mu}{\partial v}}{\frac{\partial \mu}{\partial t}}.$$

The above is to be regarded as a General Equation of State applying to all bodies, solid, liquid, or gaseous. It is the right-hand term that would be missing with the usual limiting mathematical treatment.

The Elasticity Function β/k_T.

Since by definition we have that

$$k_T = C = -\frac{1}{v}\cdot\frac{\partial v}{\partial p} = \text{compressibility constant,}$$

$$\beta = \frac{1}{v}\cdot\frac{\partial v}{\partial t} = \text{expansibility coefficient,}$$

and therefore $$\frac{\beta}{k_T} = \frac{\partial p}{\partial t}.$$

Substituting the latter in the general equation of state, it follows that

$$\frac{\beta}{k_T} = \frac{\frac{\partial \mu}{\partial v}}{\mu}\cdot\frac{\partial U}{\partial t} - \frac{1}{\mu}\cdot\frac{\partial \mu}{\partial t}\cdot\left(1 + \frac{p}{\frac{\partial U}{\partial v}}\right)\cdot\frac{\partial U}{\partial v}.$$

The quantity $p\Big/\frac{\partial U}{\partial v}$ represents the ratio of external to internal work performed at constant temperature.

From the above it is seen at once that two important limiting conditions are indicated. The one is when the body is about to change its state (as at fusion, or boiling, Edser-Lewis condition), and the other is when the body is far removed from the latter critical condition. Supplemental, therefore, to the work of Grüneisen and Ratnowsky, it is particularly significant that a general formula can be derived thermodynamically to cover both types of conditions at one and the same time.

The Grüneisen-Ratnowsky Type of Function.

At temperatures sufficiently far removed from the change of state where the function $\frac{\partial U}{\partial t}$ is naturally predominant over $\frac{\partial U}{\partial v}$ or the effect of the p-term, we have the limiting condition

$$\left.\frac{\beta}{k_T}\right|_0 \equiv \frac{1}{\mu}\cdot\frac{\partial \mu}{\partial v}\cdot\frac{\partial U}{\partial t}.$$

If, then, with Andrews, we write

V = atomic volume,

d = density,

it follows, on assuming that Dulong and Petit's law prevails, that

$$\frac{\partial U}{\partial t} \equiv \frac{6.6}{Vd},$$

so that on substitution, we have

$$\left.\frac{\beta}{k_T}\right|_0 \equiv \frac{6.6}{Vd} \cdot \frac{1}{\mu} \cdot \frac{\partial \mu}{\partial v}.$$

The latter will also lead to the Grüneisen specific heat condition

$$\left.\frac{\beta}{k_T}\right|_0 \equiv A \cdot \frac{\partial U}{\partial t},$$

provided it can be proved that

$$\frac{1}{\mu} \cdot \frac{\partial \mu}{\partial v} = \text{constant},$$

and not zero as hitherto assumed. It is precisely the former condition that is satisfied by the needed grouping of the metals according to rows, as Andrews found to be the case. The metals Fe, Ni, Zn; Ag, Sn; Au, Pt, Pb, are naturally grouped according to atomic weight, so that there was experimental justification for the statement of Andrews (see *l. c.* p. 667, footnote) "that to each of the above groups the relation $\left[\frac{V\beta}{k_T} = \psi(t)\right]$ applied separately, as an approximation which extends up to half the absolute temperature of fusion." For the exact equation see further.

The Thermodynamic Integration Factor for the Solid State.

Integrating the differential equation of condition above, we have that

$$\mu = \psi(t) \cdot \epsilon^{Av}$$

so that the Grüneisen-Ratnowsky type of formula should really read

$$\frac{V\beta}{k_T} = \frac{6.6A}{d} \cdot \psi(t),$$

and all "logical difficulty" is avoided. It is significant that the above development has not had to depend on the quantum theory and is rather supplemental than in contradiction to it.

For the solid state, therefore, we have the equation of state

$$p+\frac{\partial U}{\partial v}+\frac{\frac{\partial p}{\partial t}}{\frac{d}{dt}\lg\psi}=\frac{A}{\frac{d}{dt}\lg\psi}\,\frac{\partial U}{\partial t},$$

where ψ is a function of t only.

The Edser-Lewis Latent Heat Formula.

Turning now to conditions about the change of state where the term $\frac{\partial U}{\partial v}$ predominates over $\frac{\partial U}{\partial t}$, the elasticity function becomes

$$\left.\frac{\beta}{k_T}\right|_C\equiv-\frac{1}{\mu}\cdot\frac{\partial\mu}{\partial t}\left(1+\frac{p}{\frac{\partial U}{\partial t}}\right)\cdot\frac{\partial U}{\partial v}.$$

Thus, with Edser, writing λ for the internal heat per unit volume, it is found that practically

$$\left.\frac{\beta}{k_T}\right|_C\equiv-\lambda\,.\frac{1}{\mu}\,.\frac{\partial\mu}{\partial t}.$$

In the case of gases for which $\mu=\frac{1}{t}$, we at once arrive at the result of Edser-Lewis. More generally, if we assume

$$-\frac{1}{\mu}\cdot\frac{\partial\mu}{\partial t}=\phi(v)\,.\,F(t),$$

on integration we obtain

$$-\lg\mu=\phi(v)\,.\int Ft\,.\,dt=\phi(v)\,.\lg f(t),$$

$$\mu\,.f(t)=\phi(v).$$

Clearly for the state near the point of ebullition a more general type of function would be

$$\mu=at^m\,.\,\phi(v),$$

which on substitution would give

$$\left.\frac{\beta}{k_T}\right|_C\equiv\frac{m\lambda}{t}.$$

The Integrating Factor and the Question of Phase.

According to the above analysis the elasticity function $\frac{\beta}{k_T}$ was shown to consist of two parts, of which the one depended on $\frac{\partial U}{\partial t}$ and the second on $\frac{\partial U}{\partial v}$ primarily. Yet according to either limitation, μ consisted of two factors, $\psi(t)$ and $\phi(v)$. If then, for generality, we write as follows:

$$\mu = \psi(t) \cdot \phi(v),$$

it is quite clear that the precise form of μ as an integrating factor of the thermodynamic energy equation depends firstly upon the considered phase of the substance, and secondly on the conditions prevailing both at the change of state and at points far removed from the change of state. Naturally, for the case of a perfect gas, $\frac{\partial U}{\partial v} = 0$, and therefore $\phi(v)$ would not be present. However, for actual gases near their change of state (very low temperatures), the latent heat condition involving $\frac{\partial U}{\partial v}$ is being approached, so that the more general integrating factor μ as above given ought to be used. This condition should have material influence on the specific heat values as a function of the temperature, and can be used to explain much of Dr. Giacomini's findings recorded in the Phil. Mag. for July 1925, p. 154.

Dec. 1, 1925.

XXXV. *Eddying Flow from Annular Nozzles*[*]. *By* E. Tyler, *M.Sc.*, *and* E. G Richardson, *B.A.*, *M.Sc.*, *Ph.D.* (*University College, London*)[†].

In 1922 a paper[‡] appeared by Krüger and Marschner on the tones given out by fluid passing through a ring-shaped nozzle, formed by the space between the mouth of a cylindrical tube and a disk concentric with the tube and flush with the mouth. It was thought by the present authors that the system of embryo vortex-rings formed in the issuing

---

[*] This work was begun in 1923. The early results and deductions formed part of a Ph.D. Thesis at the Univ. of London, Jan. 1925.

[†] Communicated by the Authors.

[‡] Krüger & Marschner, *Ann. der Phys.* lxvii. p. 581 (1922).

fluid should be mainly governed by the disk, considered as an obstacle in the stream, and that the frequency of production, n, of vortices should be related to the velocity, V, of the stream by the relation: $V/nD =$ constant, D being the diameter of the disk. This relation is that found by Strouhal[*] for a cylinder in a stream, so that the tones produced would be, in fact, the Æolian Tones of a circular disk, modified possibly by the proximity of the outer tube of the nozzle—the type of nozzle is shown in fig. 1.

Krüger and Marschner's work dealt mainly with another aspect of the subject, *i.e.*, the "edge tones" produced when the vortices strike a concentric edge placed at a distance from the annular slit, but they also gave a few results at low frequency for the simple case with no edge, from which they maintained the law applying to this case to be $V/nd =$ a constant $(=18)$, ($d =$ width of slit, independent of D, the diameter of the disk). As these results seemed to be at variance with what physical notions would suggest, it was decided to examine both aspects of the problem further.

It may be pointed out that the annular mouthpiece finds application in certain sources of sound[†], in which the air issuing strikes some form of resonator, notable examples being the Galton whistle, and the "bell whistle" used on locomotives.

Cylindrical Pipes "blown" by Annular Apertures.

The nozzles or mouthpieces used were made to the design described by Krüger and Marschner. Each consisted of a hollow brass cylinder, about 10 cm. long, narrowed at one end for attachment to a rubber tube from the reservoir; a $\frac{1}{8}$ in. brass rod formed the axis of the cylinder and was kept in position by two circular plates, perforated with holes. The brass rod projected a fraction beyond the mouth of the cylinder, and the projection was threaded, so that a washer of slightly less diameter than the inside of the cylinder might be screwed down flush with the mouth, against a stop on the rod. There were two mouthpieces, one of 1·390 cm. inside diameter, provided with two interchangeable disks, 1·254 cm. and 1·200 cm. diameter respectively; the other tube of 2·883 cm. diameter, with washers 2·700 cm. and 2·500 cm. diameter. These were held in a clamp, and a pipe of thin brass tube was filed down to a bevel at the mouth, corresponding to the upper lip of an organ pipe of 1·33 cm. diameter for the smaller mouthpiece and 2·80 cm. for the larger. The pipe was set co-axially to the mouthpiece, and the distance "*f*" between nozzle and lip was measured by a travelling microscope. The blower consisted of a tall tank into which high-pressure water could be run through a regulating tap at the bottom. The only outlet for the air driven out of the tank by the water was by way of the nozzle formed in the mouthpiece, between the brass disk and the cylinder. This air impinging on the lip of the pipe at a suitable speed caused it to sound its fundamental or an overtone. The tone was purer than that of an average diapason of metal, but not so loud, though of sufficient intensity for the frequency to be estimated by comparison with a monochord, beats being easy to count; the tone of the pipe, thus excited, could be kept constant for

---

[*] Strouhal, *Ann. der Phys.* v. p. 216 (1878).

[†] First so used by Gripon, *Ann. der Phys.* viii. p. 384 (1874).

Table I.

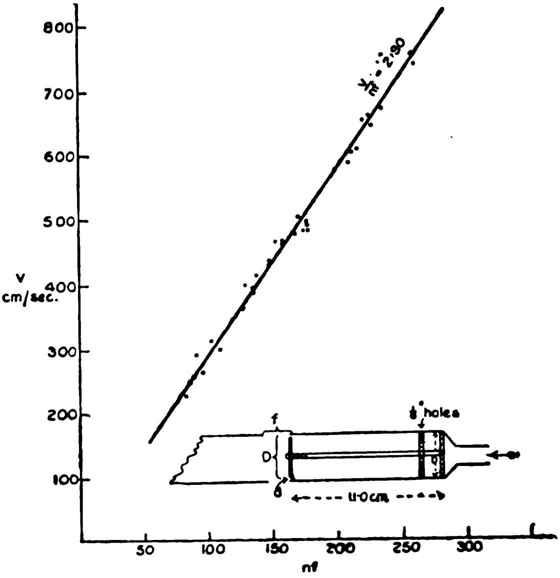
Air Results with Pipe.

Pipe D′.	D (Disk).	*d*.	*f*.	*n*.	V.	$\frac{V}{nf}$
cm.	cm.	cm.	cm.		cm./sec.	
1·390	1·254	·068	·24	620	476	3·19
			·27	950	736	2·88
			·34	365	354	2·85
			·35	500	490	2·80
			·35	372	385	2·97
			·36	475	476	2·78
			·36	640	668	2·90
			·38	376	429	3·00
			·38	763	793	2·74
			·40	553	657	2·97
			·42	370	460	2·97
			·42	500	602	2·88
			·45	502	639	2·83
			·72	186	379	2·83
1·390	1·200	·095	·34	195	496	2·82
			·34	372	392	3·11
			·42	496	582	2·80
			.42	370	454	2·90
			·52	248	364	2·83
			·52	372	525	2·73
			·58	312	518	2·86
2·883	2·700	·091(5)	·28	283	214	2·66
			·25	433	292	2·70
			·43	223	240	2·50
			·45	285	344	2·69
			·50	190	257	2·73
			·53	283	379	2·51
			·65	155	257	2·55
			·70	180	302	2·40

half a minute or more. The tank was provided with a wide glass water-gauge, so that by observing the rise in, say, 10 seconds, one could calculate the volume "v" of air delivered in that time through the nozzle of area A. Then the velocity of efflux, $V = v/10A$. Thus V, n, D, and f were all known.

The resonance curve is flat, owing to the strong damping, although finer adjustment of wind-speed is needed than that on an ordinary flue pipe. In Table I. the value of V given is that which appeared to elicit the given tone most strongly.

Fig. 1.



These results are shown on fig. 1, where it will be seen that they lie fairly on the line given by $V/nf = 2{\cdot}90$. As all the results for various values of D and d fall on the same line, it appears that these quantities have no appreciable effect on the non-dimensional quantity, V/nf. That the frequency of the pipe was the same as that of the rate of production of vortices was confirmed by mixing smoke with the air and examining the motion stroboscopically. The same value for V/nf was found by Krüger and Marschner using the circular edge, and was explained by them as follows. As each eddy strikes the edge, it sends out a wave of compression, which travels back to the nozzle with the speed of sound, starting another vortex which travels with the fluid to the edge. The distance between successive vortices thus becomes equal to f or a sub-multiple of f; f is the wave-length of a disturbance of frequency n, which travels from slit to edge. If we assume the translational velocity of the eddies to be always a constant fraction a of V, then $V/nf=a$. The pipe and the eddy system are accordingly "coupled" in the acoustic sense. Experiments in water in which a stream of liquid from a nozzle struck a small length of pipe seemed to show that unless the natural period of the pipe as resonator coincided with that of the vortices, the distance between successive vortices in each row was not forced into coincidence with f; at any rate, with the adjustment possible in the apparatus, no such effect was observed, nor with smoke in air, except at resonance.

Results without Pipe—in Water.

Attention was now turned to the more important case—to us—of the frequency of the eddying produced by outflow from the nozzle into a clear space. Water seemed more amenable as fluid, and previous experiments[*] on æolian tones had taught us that viscosity was not likely to influence the period of the motion. In order to examine the motion, the issuing fluid was coloured with Meldola's Blue, and the nozzles submerged mouth downwards in a rectangular tank of 10 litres capacity, filled with clear water. V was measured by collecting the water from an overflow pipe, which met the surface of the liquid normally near the top of the tank; n was found by two methods—(1) by counting (when less than 6 per sec.), (2) by looking through a stroboscopic disk. The use of the stroboscope for examining a motion such as this, which, though periodic, does not exactly repeat itself in space, is difficult, but with practice was found to give results in agreement with the first method over the range where they were both applicable (*vide* fig. 2).

The problem of the dependence of the eddy frequency on the dimensions of the nozzle was attacked from two directions. At first, disks of different diameter were used in three nozzles previously described; this meant that both D and d varied. Subsequently a fixed disk was used, outer tubes of different diameters being clamped round it, so that d varied while D was constant.

---

[*] Richardson, Proc. Phys. Soc. xxxvi. p. 153 (1924).

The graphs show that there is a critical velocity V_c for each value of *d*, below which the fluid emerges in a steady stream. From velocities a little above the critical, the relation between V and *n* becomes linear, the slope, $\frac{\delta V}{\delta n}$, of the line decreasing as *d* increases, tending to a limiting

Fig. 2.

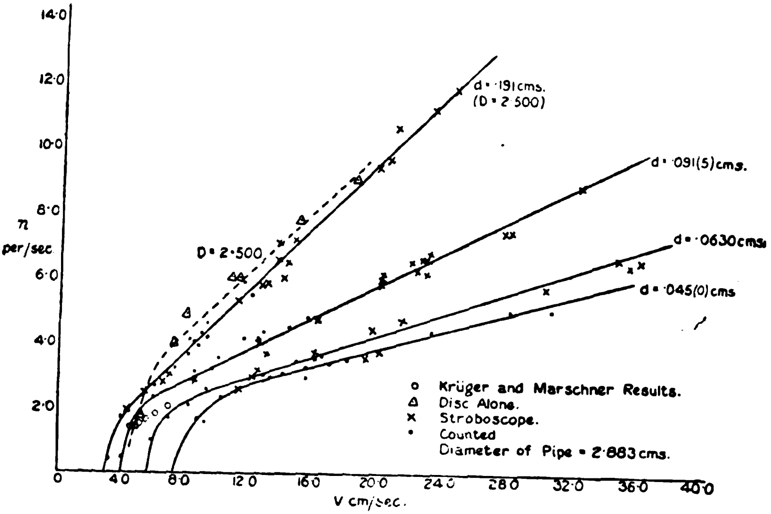


Fig. 3.

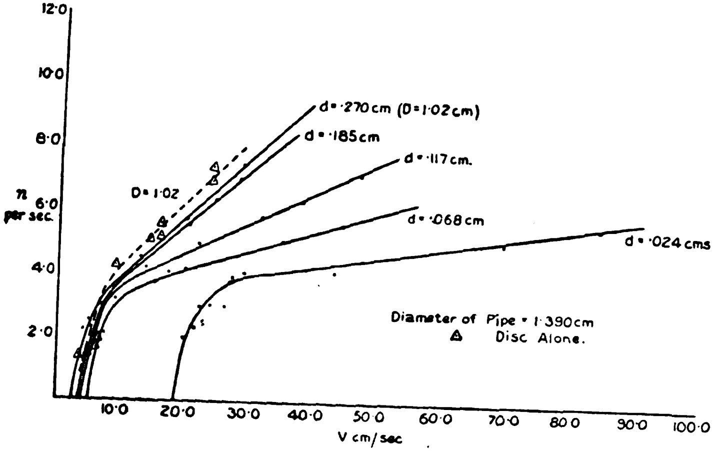


Fig. 4.

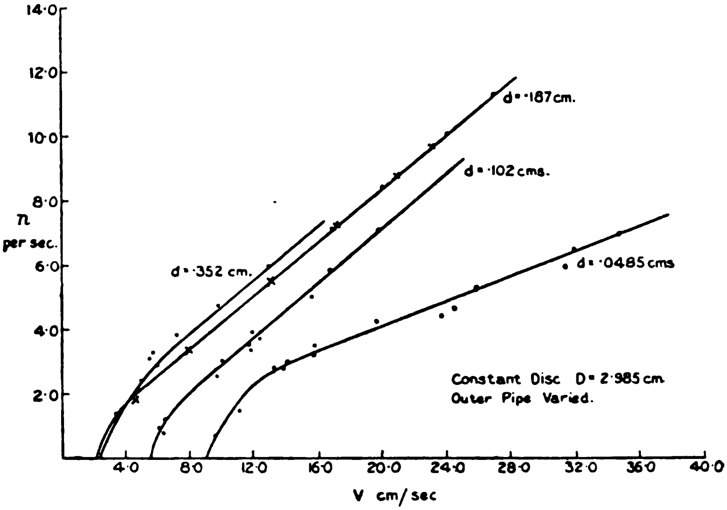
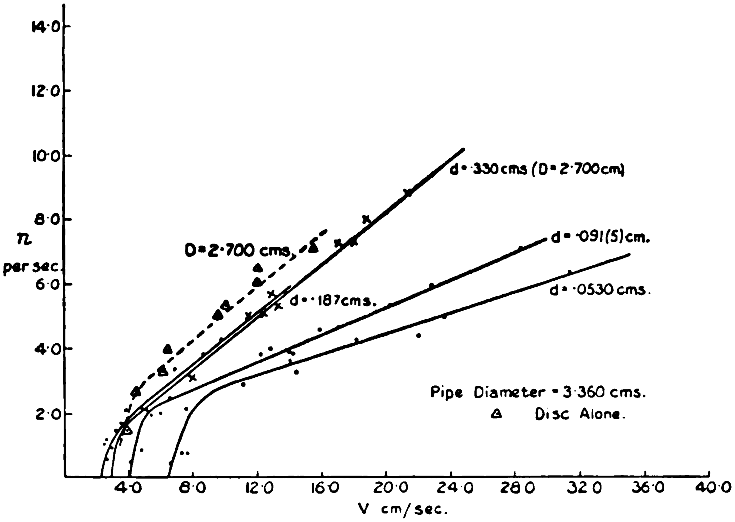


Fig. 5.



constant slope when *d* reaches 2 mm. The critical velocity is inversely as *d*, and practically independent of the disk. This indicates a Reynolds' Number of about 40 as the limit for steady motion in the slit. The graph (fig. 7) includes a few measurements of V in air (mixed with magnesium oxide smoke).

Fig. 6.

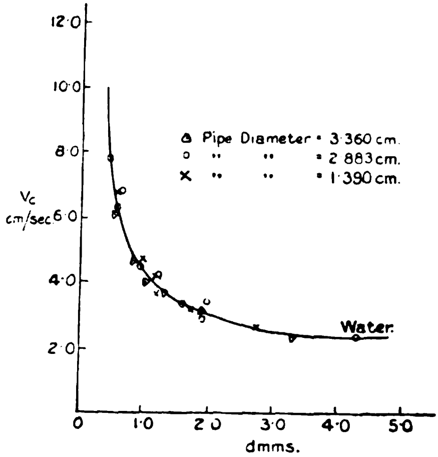
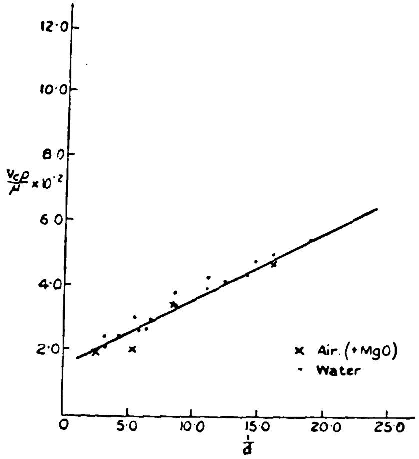


Fig. 7.



Results without Pipe—in Air.

It is difficult to draw any conclusions from observations of air mixed with smoke in the absence of a resonator. The periodic heating and cooling of a hot wire, however, serves to indicate the period of the eddy production, as was shown by Relf & Simmonds [*], who succeeded in thus measuring the value of V/*n*D for a cylindrical rod past which air is streaming. The wire is heated electrically until nearly red-hot, and is coupled to a shunted vibration galvanometer through a transformer. The galvanometer is tuned to maximum resonance with the period of heating and cooling of the wire, and for determining the corresponding frequency we calibrated the galvanometer with the intermittent current from a make-and-break of the vibrating reed type; the length of the reed was varied, and its frequency found by means of the stroboscope. This was in place of Relf's method of speeding-up an alternator to the desired frequency. The range of *n* in our experiments was from 30 to 100. The wire consisted of an inch of ·001 in. platinum, mounted horizontally over part of the annular slit. This method does not lead to such accurate results as that of visual observation, as the hot-wire system is not sufficiently sensitive. Results are shown in Table II., and also on fig. 8.

TABLE II.

Pipe D'.	D (Disk).	*d*.	$\frac{d}{D} \times 10^2$.	$\frac{\delta V}{\delta n}$.	$\frac{\delta V}{\delta n} \cdot \frac{1}{D}$.
cm.	cm.	cm.			
2·883	2·793	·045	1·61	6·80	2·43
	2·700	·091	3·37	5·00	1·85
	2·500	·191	7·65	2·54	1·01
	2·008	·437	21·90	1·66	·79
3·360	3·253	·053	1·63	8·57	2·65
	3·198	·081	2·54	6·60	2·07
	3·157	·101	3·21	4·00	1·27
	2·985	·187	6·25	3·26	1·09

Explanation of V : *n Curves.*

The fact that, when the width of the slit is considerable, the slope of the linear part of the V : *n* curve tends to a constant limit, confirms our earlier suggestion that, when the circumference of the disk is at a moderate distance from the outer tube, we are observing the æolian eddies due to the disk placed in the path of the issuing stream. The increase in the slope of these curves as the slit gets smaller must then be attributed to the proximity of the outer walls. The effect is similar to the "interference" due to the walls of a wind-channel encountered in model experiments in aeronautics.

To confirm these conclusions, values of V and *n* for a disk in an open channel were obtained. In default of a proper water-channel, a large bowl full of water was made to revolve, while the disk was held below the water and normal to the rotating fluid. Blue liquid, fed in behind the disk, made the vortices visible ; and V was found by timing dust particles in the water. This was a rough method, but the results for these disks fell, within the accuracy of the experiment, on the previous V : *n* curves for wide slits (exceeding 2 mm.) (*vide* figs. 2, 3, 5 : dotted lines).

---

[*] Relf & Simmonds, Phil. Mag. xlix. p. 509 (1925).

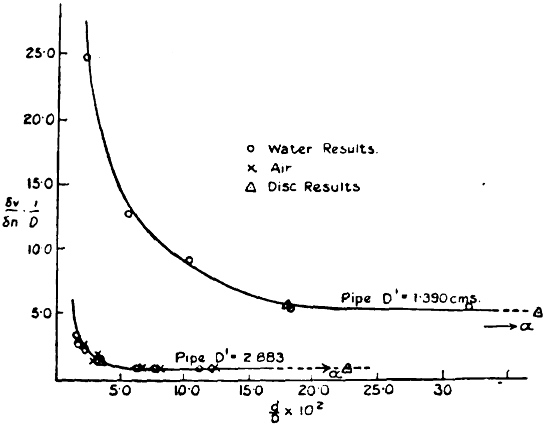
It is of interest to see why Krüger and Marschner were led to a wrong conclusion in this respect. By some misfortune, their results cover just that small part of the curve, near the critical velocity (*vide* fig. 2), where V/*nd* might be considered constant. The more extended results given here show that this is an anomalous region, the main range of the phenomenon being expressible in terms of Æolian Tones.

Theory.

If we regard the phenomenon as an Æolian Tone effect, modified by interference of the outer tube of the nozzle, we must adopt a formula of the type

$$\frac{\delta V}{\delta n}\frac{1}{D}\cdot\phi\left(\frac{d}{D}\right) = \text{constant.} \quad . \quad . \quad . \quad . \quad (1)$$

Fig. 8.



The form of the function $\phi\left(\frac{d}{D}\right)$, which expresses the influence of the boundary, may be determined by plotting $\frac{\delta V}{\delta n}\frac{1}{D}$ against $\frac{d}{D}$. This is done in fig. 8.

The results then fall onto two curves : one for the disks used in the narrow nozzle, and one for those in the wider nozzles. (It was impossible to use the set of small disks in the wide tubes owing to the impossibility of getting symmetrical flow when d exceeds 4 mm.) That all the results do not fall on an unique curve, though each curve has the same shape, is due to lack of constancy in V/nD, even in the open channel. Cylinders in the form of narrow wires exhibit an anomalous high value of V/nD *. To account for this, it is usual, following Lord Rayleigh, to multiply $\frac{\delta V}{\delta n}\frac{1}{D}$ by a function of VD/ν, and such a function would need to be included as a factor in equation (1) to make this equation universally applicable. Only having the two curves, we cannot satisfactorily determine the form of this function, but probably the viscous term would only affect results for small disks.

The relation between $\frac{\delta V}{\delta n}\cdot\frac{1}{D}$ and $\frac{d}{D}$ for either curve of fig. 8 is approximately $\frac{\delta V}{\delta n}\cdot\frac{1}{D}\times\frac{d}{D}=$ constant, for small values of d. So that equation (1) becomes, for narrow slits

$$\frac{\delta V}{\delta n}\cdot\frac{d}{D^2}=K_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

and for wide slits, simply

$$\frac{\delta V}{\delta n}\frac{1}{D}=K_2,$$

where K_1 and K_2 involve $\frac{VD}{\nu}$ when the diameters of the disks are small.

As regards the influence of the circular edge used in the acoustic observations, we may accept the sound-wave explanation, or we may look for an explanation in the "secondary" eddies produced by friction of the fluid on the sides of the edge. These appear as vortex-rings, alternately one inside and one outside the ring-shaped edge, lying between the vortices arriving from the nozzle, and rotating in the opposite sense. Karman † has shown mathematically that in a series of alternate vortices in a double row, h/l must be a constant for maximum stability, where $l=$ distance between those in a row, and $h=$ distance between the rows (*i. e.*, difference of radii of rings). As the vortices recede from the orifice, h and l are seen to increase, so that the greater the distance from slit to edge, the greater is the separation between the (primary) vortices striking the edge. As the secondary eddies have to take their places between the primary ones, this means that l and h, for the set of eddies along the sides of the edge, increase with f. This seems to react in some way on the production of the primary eddies at the nozzle, particularly when some suitable resonator is present. This would account for the reduction of n as f increases, and as V/nf is found to be constant, it would appear that h and l are always proportional to f, which implies that the separation of successive eddies increases regularly with distance from the slit.

---

* Richardson, *loc. cit.*

† Karman, *Gött. Nach.* 1912, p. 547.

This is a tentative suggestion, but is confirmed in part by photographs of eddies produced when water from a linear slit strikes a straight edge*. Such photographs show the secondary vortices plainly; on measuring these photographs we find that the eddies along the edge are closer together when the latter is near the slit. We find the same effect in photographs we have obtained using the annular slit and edge. A recent Paper† has shown that the boundaries of the eddy tracks open out regularly, in the case of the straight slit and edge; (over a considerable range, h, and therefore l, is directly as f).

Summary.

The conclusions of Krüger and Marschner on their work on the frequency of eddies produced in the flow from annular slits require modification. Whereas they ascribe the characteristics of the motion to the width of the slit, we claim to show that the motion once started is governed by the diameter of the disk, modified by the width of the slit, when the latter is small (less than 2 mm. in those we examined). It is, in fact, the Æolian Tone phenomenon of a disk, modified by the outer boundary of the nozzle. There is a critical velocity for the commencement of the eddying flow, which is governed by the slit; but a little above this, at another critical velocity, the pendulation is governed by the size of the disk.

When the eddies strike a circular edge, the results of Krüger and Marschner are confirmed; the distance between successive vortices becomes equal to, or a sub-multiple of, the distance from slit to edge. This is ascribed to the secondary eddies produced at the edge itself.

In conclusion, we wish to give our best thanks to Prof. A. W. Porter, D.Sc., F.R.S., for putting the necessary facilities at our disposal and for encouragement during the course of this research.

---

* Schmidtke, *Ann. der Phys.* lx. p. 742 (1919).

† Benton, Proc. Phys. Soc. xxxviii. p. 114 (1926).

XXXVI. *Some Considerations of the Reaction Constant Equation, and a Simple Method of Determining the End Point.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

THE method of determining the end point and velocity constant of a monomolecular reaction from two values obtained at specified times such that one time is half the other, which is described by Mr. Robert Christie Smith in your issue, 7th ser. vol. i. p. 496 (1926), was previously developed by Dr. L. N. G. Filon in a somewhat different form, and is described in 'Investigations on the Theory of Photographic Process," by S. E. Sheppard and C. E. K. Mees, p. 65 (Longmans, Green & Co., 1907). The method has been in continued use in practical sensitometry since then.

Using Mr. Smith's nomenclature, the equation $1/t \log \frac{T_\infty}{T_\infty - T} = k$ may be written $T = T_\infty (1 - e^{-kt})$. If T_n and T_{n+1} are chosen so that $t_{n+1} = 2t_n$, then

$$T_n = T \quad (1 - e^{-kt_n}), \quad . \; . \; . \; . \; . \; . \; . \quad (a)$$

$$T_{n+1} = T \quad (1 - e^{-kt_{n+1}}) \; ; \quad . \; . \; . \; . \; . \quad (b)$$

and putting $e^{-kt_n} = x$, we have from (*a*) and (*b*)

$$\frac{T_n}{T_{2n}} = \frac{1 - x}{(1 - x^2)} = \frac{1}{1 + x} = \frac{1}{1 + e^{-kt_n}} \; ;$$

hence
$$\frac{T_{2n} - T_n}{T_n} = e^{-kt_n}$$

and
$$k = \frac{1}{t_n} \log \frac{T_n}{T_{2n} - T_n},$$

which gives k, and T_∞ may be obtained by substitution.

Mr. Smith's deduction of this method is obviously entirely independent, and is valuable in drawing attention to it anew and commending it to a wider field of utility.

Very truly yours,
S. E. SHEPPARD,
Assistant Director of Research.

Eastman Kodak Company,
Rochester, N.Y.
10 April, 1926.

XXXVII. *Temperature Stresses and Deflexions in the Fins and Barrel of an Air-cooled Internal Combustion Engine Cylinder.* *By* A. M. BINNIE, *M.A. Cantab.**

SUMMARY.

IN the following paper an attempt is made to evolve a method of calculating the temperature stresses and deflexions in the barrel and radial fins of an air-cooled internal combustion engine cylinder. For the simple case considered it is shown

(1) That much weight can be saved by reducing the thickness of the fins towards their tips. The decrease in cooling power and the increase in temperature stress, which ensue, are both negligibly small.

(2) That the spacing of the fins is of importance. To avoid distortion of the cylinder barrel the fins should be placed as near together as possible compatible with facility of casting.

(3) That to a small extent the temperature stresses in the fins assist the barrel to withstand the internal pressure in the cylinder.

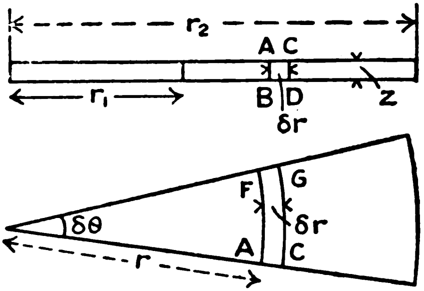
Introduction.

TO avoid complexity, the theoretically perfect case is considered, in which a hot cylinder is steadily giving out heat solely by radiation to its surroundings and obeying Newton's Law of Cooling. The fin is supposed to be thin so that for points equidistant from the cylinder axis the stresses and shift are constant.

In the first instance the fins alone will be considered.

Fin of Constant Thickness.

Fig. 1.



Consider the fin depicted in fig. 1. Taking the element whose plan and elevation are shown by AFGC and ABCD respectively, the heat-flow outwards across AB is

---

* Commuicated by the Author.

$$-\mathrm{K}\,.\,r\,.\,\delta\theta\,.\,z\,.\,\frac{d\mathrm{T}}{dr},$$

where K is the coefficient of conduction and T the temperature at radius r measured above that of the surroundings. The heat-flow outwards across CD is

$$-\mathrm{K}(r+\delta r)\delta\theta\,.\,z\,.\,\frac{d}{dr}\left(\mathrm{T}+\frac{d\mathrm{T}}{dr}\,.\,\delta r\right).$$

The loss of heat by radiation is $2e.\mathrm{T}\,.\,r.\delta\theta.\delta r$ where e is the coefficient of emissivity. Hence, equating and simplifying, the T-r relation is given by the equation

$$\frac{d^2\mathrm{T}}{dr^2}+\frac{1}{r}\,.\,\frac{d\mathrm{T}}{dr}-\frac{2e\mathrm{T}}{\mathrm{K}z}=0,$$

of which the solution is

$$\mathrm{T}=\mathrm{AJ}_0\left(ri\sqrt{\frac{2e}{\mathrm{K}z}}\right)+\mathrm{BH}_0\left(ri\sqrt{\frac{2e}{\mathrm{K}z}}\right).$$

A and B are constants given by the relations that at $r=r_1$, $\mathrm{T}=\mathrm{T}_1$, and at $r=r_2$, $\frac{d\mathrm{T}}{dr}=0$.

For a short fin the loss of heat from the tip becomes of importance, and a trial and error procedure is necessary, the two constants being chosen so that at $r=r_1$, $\mathrm{T}=\mathrm{T}_1$, and at $r=r_2$, $\frac{d\mathrm{T}}{dr}=-\frac{\mathrm{E}z\mathrm{T}_2}{\mathrm{K}}$. In all practical cases, however, this further complication is an unessential refinement.

Proceeding to a consideration of the temperature stresses, let u, p, and t be the shift, radial tensile stress, and hoop tensile stress respectively at radius r. The fin is assumed thin, so that there are no appreciable longitudinal stresses. Then the stress-strain relations are given by

$$\mathrm{E}\left(\frac{du}{dr}-k\mathrm{T}\right)=p-\frac{t}{m}$$

and

$$\mathrm{E}\left(\frac{u}{r}-k\mathrm{T}\right)=t-\frac{p}{m},$$

and the equation of equilibrium of the element by

$$p-t+r\,.\,\frac{dp}{dr}=0,$$

k being the coefficient of thermal expansion, E Young's

Modulus, and m Poisson's Ratio. Hence, using the temperature relation already found,

$$p = \frac{iEk}{r\sqrt{\frac{2e}{Kz}}}\left[AJ_1\left(ri\sqrt{\frac{2E}{Kz}}\right)+BH_1\left(ri\sqrt{\frac{2E}{Kz}}\right)\right]+\frac{F}{2}+\frac{D}{r^2},$$

F and D being constants determined by a knowledge of the radial pressures existing at the root and tip of the fin. It will be noticed that the terms involving F and D are the same as those which give the distribution of radial stress in a fin whose temperature is the same throughout. Further,

$$t = F - EkT - p, \quad \text{and} \quad u = \frac{r}{E}\left[F - p\left(1+\frac{1}{m}\right)\right].$$

Fin of Varying Thickness.

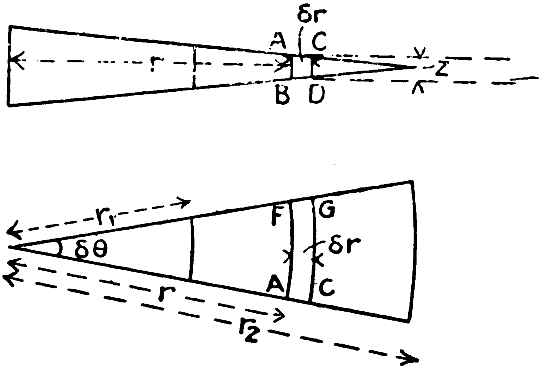
Using the same notation and considering the element shown in fig. 2, it is evident that the heat-flow outwards across AB is

$$-K\,.\,r\,.\,\delta\theta\,.\,z\,\frac{dT}{dr},$$

and across CD is

$$-K(r+\delta r)\,\delta\theta\left(z+\frac{dz}{dr}\,\delta r\right)\frac{d}{dr}\left(T+\frac{dT}{dr}\,\delta r\right).$$

Fig. 2.



The heat lost by radiation is $2\,.\,\delta r\,.\,\delta\theta\,.\,e\,.\,T\,.\,r$, if $\frac{dz}{dr}$ may be assumed small. Hence the T-r relation is

$$\frac{d}{dr}\left(zr\frac{dT}{dr}\right)+2eTr = 0.$$

The constants in the solution of this equation are found, as before, from the facts that at $r=r_1$, $T=t_1$, and at $r=r_2$, $\frac{dT}{dr}=0$. If extreme accuracy is desired, the second condition should be that at $r=r_2$, $\frac{dT}{dr}=\frac{-ezT}{K}$.

Consider in the first instance a fin whose thickness varies inversely as the radius. If $z=\frac{\lambda}{r}$, λ being a constant, the equation connecting T and r becomes

$$\frac{d^2T}{dr^2}-PTr=0, \quad \text{where} \quad P=\frac{2e}{\lambda K}.$$

The solution of this is

$$T=r^{\frac{1}{2}}\left[AJ_{\frac{1}{3}}\left(\tfrac{2}{3}iP^{\frac{1}{2}}x^{\frac{3}{2}}\right)+BJ_{\frac{1}{3}}\left(\tfrac{2}{3}iP^{\frac{1}{2}}x^{\frac{3}{2}}\right)\right],$$

where A and B are constants; but a solution in a form more convenient in the subsequent stress determinations can be found without the aid of Bessel Functions. Let

$$T=a_0+a_1r+a_2r^2+\ldots+a_nr^n.$$

Then, by equating coefficients of like powers of r,

$$T=a_0\left[1+\frac{Pr^3}{6}+\frac{P^2r^6}{180}+\frac{P^3r^9}{12960}\cdots+\cdots\right]$$
$$+a_1r\left[1+\frac{Pr^3}{12}+\frac{P^2r^6}{504}+\frac{P^3r^9}{45360}+\cdots\right],$$

a series which is seen to be convergent. Since P is in most cases small *, it is sufficient to take

$$T=a_0\left[1+\frac{Pr^3}{6}\right]+a_1r\left[1+\frac{Pr^3}{12}\right],$$

the constants being determined as before.

The stress-strain relations are again

$$E\left(\frac{du}{dr}-kT\right)=p-\frac{t}{m}$$

and

$$E\left(\frac{u}{r}-kT\right)=t-\frac{p}{m},$$

and the equation of equilibrium $zt=\frac{d}{dr}(zrp)$ becomes

$$t=r\frac{dp}{dr}.$$

---

* In the numerical example taken, $P=\cdot 00069639$ and the maximum value of Pr^3 is $\cdot 50767$.

Eliminating and simplifying, the p-r equation is given by

$$r^2\frac{d^2p}{dr^2}+2r\frac{dp}{dr}-p\left(1+\frac{1}{m}\right)=-r\mathrm{E}k\left(\frac{\mathrm{P}r^3}{2}a_0+a_1\left(1+\frac{\mathrm{P}r^3}{3}\right)\right).$$

The complete solution of this is

$$\mathrm{P} = \mathrm{Y}_1r^{\cdot 745}+\mathrm{Y}_2r^{-1\cdot 745}+\alpha r+\beta r^3+\gamma r^4,$$

where

$$\alpha=\frac{-\mathrm{E}ka_1}{\cdot 7},$$

$$\beta=\frac{-\mathrm{E}k\mathrm{P}a_0}{21\cdot 4},$$

$$\gamma=\frac{-\mathrm{E}k\mathrm{P}a_1}{56\cdot 1},$$

and Y_1 and Y_2 are constants. $m=\frac{10}{3}$.

Similarly,

$$t = \cdot 745\mathrm{Y}_1r^{\cdot 745}-1\cdot 745r^{-1\cdot 745}+\alpha r+3\beta r^3+4\gamma r^4$$

and

$$u = \frac{r}{\mathrm{E}}[\cdot 445\mathrm{Y}_1r^{\cdot 745}-2\cdot 045r^{-1\cdot 745}+\cdot 7\alpha r+2\cdot 7\beta r^3 + 3\cdot 7\gamma r^4+\mathrm{E}k\mathrm{T}].$$

To compare with these results the further case has been taken of a fin whose thickness varies inversely as the square of the radius. Taking $z=\frac{\lambda}{r^2}$, the general equation becomes

$$\frac{d}{dr}\left(\frac{1}{r}\cdot\frac{d\mathrm{T}}{dr}\right)=\frac{2e}{\lambda\mathrm{K}}\cdot\mathrm{T}r,$$

of which the solution is

$$\mathrm{T} = \mathrm{A}\sinh \mathrm{F}r^2+\mathrm{B}\cosh \mathrm{F}r^2,$$

where $\mathrm{F}=\sqrt{\frac{e}{2\lambda\mathrm{K}}}$ and A and B are constants. Proceeding in a manner similar to that used previously, p is found to be given by the equation

$$r^2\frac{d^2p}{dr^2}+r\frac{dp}{dr}-2p\left(1+\frac{1}{m}\right) = -2\mathrm{E}k\mathrm{F}r^2(\mathrm{A}\cosh \mathrm{F}r^2+\mathrm{B}\sinh \mathrm{F}r^2).$$

The particular integral of this equation cannot be found exactly in a convenient form; but since F is small, $\sinh \mathrm{F}r^2$ and $\cosh \mathrm{F}r^2$ can be expanded and a solution obtained to any desired degree of accuracy[*]. If the bracket in the right-hand side of the above equation be taken as $A\left(1+\frac{F^2r^4}{2}\right)+BFr^2$, then

$$p = Y_1r^{1\cdot612}+Y_2r^{-1\cdot612}+\alpha r^2+\beta r^4+\gamma r^6,$$

where

$$\alpha = -\frac{A}{1\cdot4}\,.\,2EFk,$$

$$\beta = -\frac{BF}{13\cdot4}\,.\,2EFk,$$

$$\gamma = -\frac{AF^2}{66\cdot8}\,.\,2EFk,$$

and Y_1 and Y_2 are constants.

Further,

$$t = \cdot612Y_1r^{1\cdot612}-2\cdot612Y_2r^{-1\cdot612}+\alpha r^2+3\beta r^4+5\gamma r^6$$

and

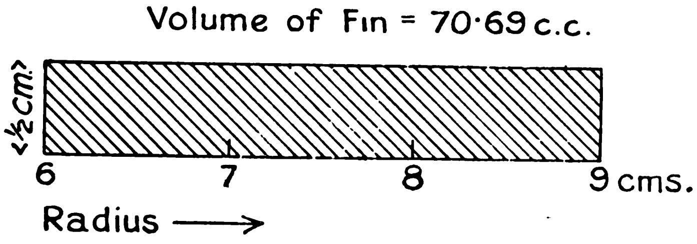
$$u = \frac{r}{E}\left[\cdot312Y_1r^{1\cdot612}-2\cdot912Y_2r^{-1\cdot612}+\cdot7\alpha r^2+2\cdot7\beta r^4 + 4\cdot7\gamma r^6+EkT\right].$$

It will be seen that in general it is impossible to determine the stresses for any given shape of fin, since it is always necessary to solve two dependent differential equations—the T-r equation and the p-r equation.

Curves (figs. 3–12) are shown, giving the temperature and stress variations in each of the three forms of fin considered, which are supposed of cast iron. In each case, the inner and outer radii are 6 and 9 cm. respectively, the fin thickness at its root is 0·5 cm., the fin temperature at its root is 400° C., the temperature of the surroundings is 0° C., and the fin is assumed to be unconstrained at both root and tip.

Fin of Constant Thickness.

Fig. 3.—Cross-section of Fin.



---

[*] In the numerical example taken, F=·0054 ; and the maximum value of Fr^2 used is ·43632, for which sinh Fr^2=45030, cosh Fr^2=1·09670, and $(1+F^2r^4/2)$=1·09519. The effect of the approximation on the temperatures in the fin is shown in fig. 11.

Fig. 4.—Temperature Drop in Fin.

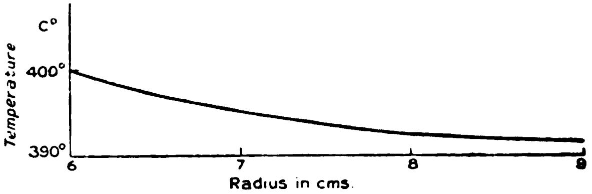


Fig. 5.—Radial Compressive Stress.

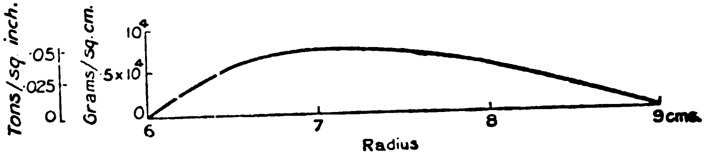
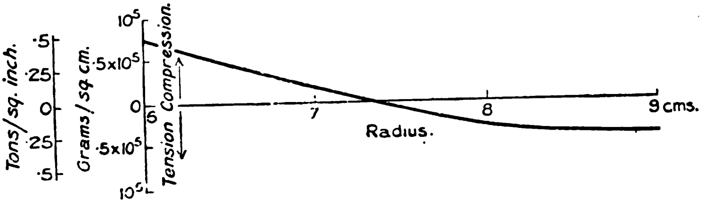


Fig. 6.—Hoop Stress.



FIN WHOSE THICKNESS VARIES INVERSELY AS THE RADIUS.

Fig. 7.—Cross-section of Fin.

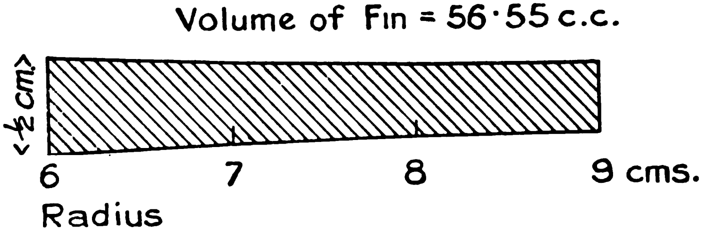


Fig. 8.—Temperature Drop in Fin.

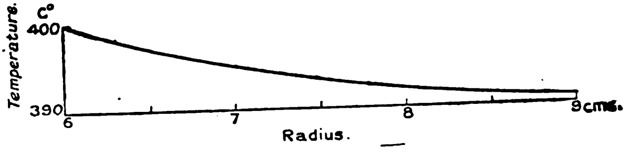
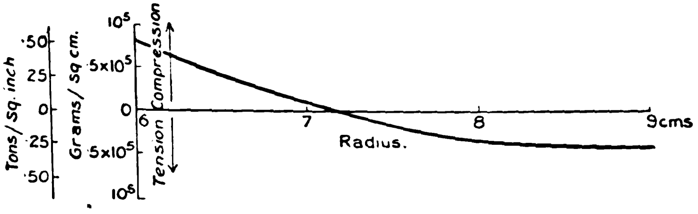


Fig. 9.—Hoop Stress.



FIN WHOSE THICKNESS VARIES INVERSELY AS THE SQUARE OF THE RADIUS.

Fig. 10.—Cross-section of Fin.

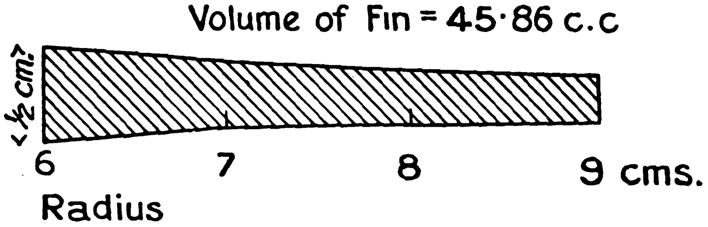
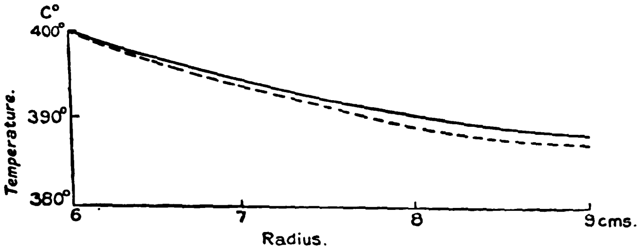
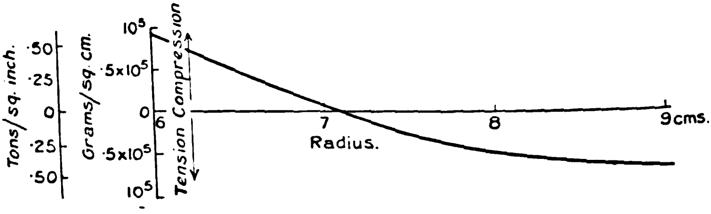


Fig. 11.—Temperature Drop in Fin.



Full line shows Exact Temperature, and broken line shows Approximate Temperature taken.

Fig. 12.—Hoop Stres



The radial pressure curve for the first case only is shown, as it is found that this stress varies but slightly with the shape of the fin and is in any case negligibly small.

These three sets of curves are intended to indicate the order of the stresses developed, and to show to what extent the temperature drops and the stresses increase when the weight of the fin is diminished by a reduction in its thickness towards the tip. It will be seen that the stresses are in no case large and do not increase inordinately when the fin thickness is diminished. The amount of heat dissipated in each case does not materially alter, varying as it does from 16·73 calories per second for the first type to 16·65 calories per second for the third, although the decrease in the weight of the fin is 35 per cent.

The Physical Constants used are:

Coefficient of Emissivity
= ·00015 calorie per second per sq. cm. per degree centigrade.

Coefficient of Conductivity
= ·1436 calorie per second per sq. cm. per degree centigrade per cm.

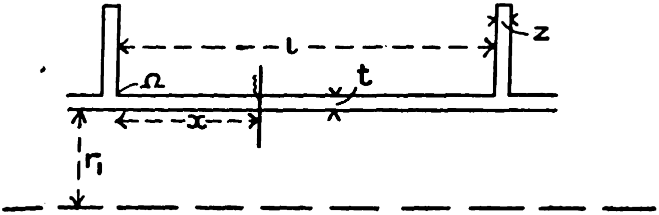
Young's Modulus
$= 1{\cdot}25 \times 10^9$ grammes per sq. cm., equivalent approx. to 8000 tons per sq. inch.

Coefficient of Linear Expansion
$= 10{\cdot}8 \times 10^{-6}$ per degree centigrade.

Stresses and Displacements in a Cylinder Barrel.

After the stresses and shifts in a single fin have been determined, it is possible by means of an extension of Professor Cook's method * to find the stress distribution

Fig. 13.



---

* Professor Gilbert Cook, D.Sc., "The Distribution of Stress in a Flanged Pipe." Complex Stress Distributions in Engineering Materials. Committee's Report, British Association, 1921. See also Von Sanden, 'Engineering,' Jan. 18th, 1924, p. 87, and Feb. 8th, 1924, p. 173.

and displacements in a cylinder barrel carrying a number of these fins equally spaced. (Fig. 13.)

Let t be the thickness of the barrel assumed small in comparison with r_1 the mean radius;
y „ the radial displacement of the wall;
q „ the tensile circumferential stress;
f „ the tensile longitudinal stress in the barrel at any point distant x measured along the axis from the fixed point Ω;
P_1 „ the internal pressure;
z_0 „ the root thickness of the fins;
T_1 „ the temperature of the barrel, which is equal to the fin root temperature.

The stress-strain relation gives

$$E\left(\frac{y}{r_1}-kT_1\right)=q-\frac{f}{m}; \text{ but } f=\frac{r_1P_1}{2t}.$$

Hence

$$q=E\left(\frac{y}{r_1}+\frac{P_1r_1}{2tmE}-kT_1\right).$$

Considering the equilibrium of a longitudinal strip of the barrel subtending an angle $\delta\phi$ at the axis. the load per unit length due to the internal pressure is $P_1r_1\delta\phi$ and due to circumferential stress is $qt\delta\phi$; so that the total load w per unit length is $P_1r_1\delta\phi-qt\delta\phi$. The equation connecting load and displacement is

$$\beta\frac{d^4y}{dx^4}=w,$$

where β is the flexural stiffness, which in this case is $\frac{m^2}{m^2-1}\cdot E\cdot\frac{1}{12}r_1\delta\phi t^3$. Hence, equating and simplifying,

$$\frac{d^4y}{dx^4}+4n^4y=b,$$

where

$$4n^4=\frac{12}{t^2r_1^2}\cdot\frac{m^2-1}{m^2},$$

$$b=\frac{12}{Er_1t^3}\cdot\frac{m^2}{m^2-1}\left[P_1r_1\left(1-\frac{1}{2m}\right)+EkT_1t\right],$$

and

$$\frac{b}{4n^4}=P_1\left(1-\frac{1}{2m}\right)\frac{r_1^2}{ET}+r_1kT_1$$

$= y_1$, the radial displacement of the barrel without fins.

The solution of this equation is

$$y = y_1 + \cos nx\,(\mathrm{A}\cosh nx + \mathrm{B}\sinh nx)$$
$$+ \sin nx\,(\mathrm{C}\cosh nx + \mathrm{D}\sinh nx),$$

where the four constants can be found from the facts that $x=0$ and $x=6$, $\frac{dy}{dx}=0$ and $y=y_0$, the radial displacement of the root of the fin. It is assumed that under the fin the barrel is held so that no angular movement is permitted. Hence

$$y = y_1 - (y_1 - y_0)[\cosh nx \cos nx - \mathrm{H}\sinh nx \cos nx$$
$$+ \mathrm{H}\cosh nx \sin nx - \mathrm{L}\sinh nx \sin nx],$$

where

$$\mathrm{H} = \frac{\cosh nl - \cos nl}{\sinh nl + \sin nl},$$

and

$$\mathrm{L} = \frac{\sinh nl - \sin nl}{\sinh nl + \sin nl}.$$

It now remains to determine y_0. Let the shearing force in the barrel at Ω be F per unit length measured along the circumference, acting outwards on the fin. Then the equivalent pressure on the fin is $\mathrm{P}_1 + \frac{2\mathrm{F}}{z_0}$.

But
$$\mathrm{F} = -\mathrm{E}\,.\,\frac{m^2}{m^2-1}\,.\,\frac{t^3}{12}\,.\left(\frac{d^3y}{dx^3}\right)_{x=0}.$$

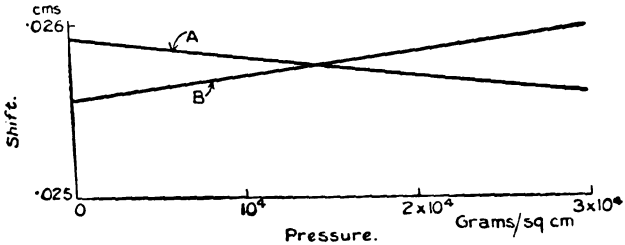
Hence P_2, the equivalent pressure,

$$= \mathrm{P}_1 + \frac{2\mathrm{E}}{3z_0}\,.\,\frac{m^2}{m^2-1}\,.\,t^3n^3(y_1-y_0).$$

Therefore for any particular cylinder and under given conditions of temperature and internal pressure, a curve connecting P_2 and y_0 may be drawn. It has been shown how, for any of the fins whose stress distributions and shift functions have been investigated, a curve may be drawn connecting p_1 the internal pressure and u_{r_1} the displacement at the root of the fin. But P_2 must equal p_1 and y_0 must equal u_{r_1}. Hence the point of intersection of the two curves will give these four quantities; and when these are known, all the stresses and displacements both in the fin and in the barrel can be determined.

Figs. 14–21 have been calculated for a cast-iron barrel, ·5 cm. thick and 6 cm. mean radius, on which are cast a

Fig. 14.—Determination of Pressure between Fin and Barrel.

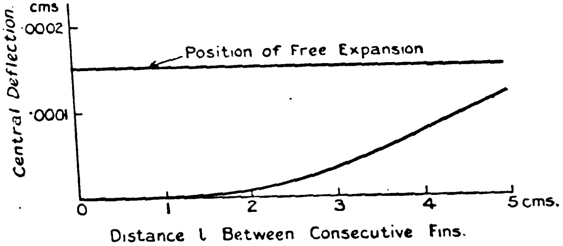


Curve A shows relation between Pressure and Deflexion of Cylinder Barrel.

Curve B shows relation between Pressure and Deflexion of Root of Fin.

Pressure between Fin and Barrel =14·500 grams/sq.cm.
=1/10 ton/sq. inch approx.

Fig. 15.—Deflexions of Points midway between adjacent Fins for varying Fin Spacings.



Deflexions are measured from final position of Root of Fin.
Deflexion of Root of Fin = ·02577/cm.

Fig. 16.—Compressive Circumferential Stress at Points midway between adjacent Fins for varying Fin Spacings.

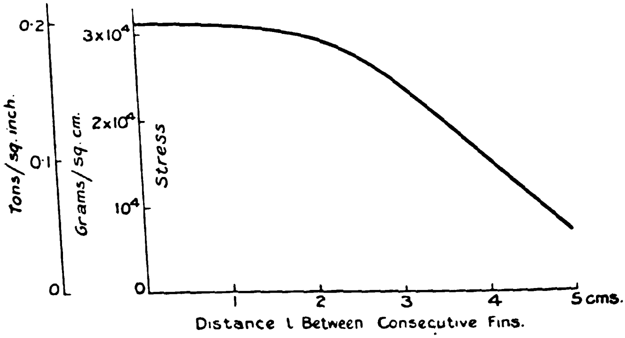


Fig. 17.—Deflexion of Barrel relative to Roots of Fins when Fins are 1 cm. apart.

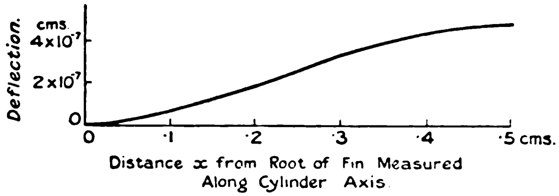


Fig. 18.—Deflexion of Barrel relative to Roots of Fins when Fins are 2 cm. apart.

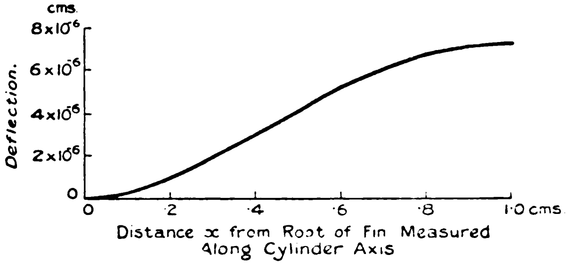


Fig. 19.—Deflexion of Barrel relative to Roots of Fins when Fins are 3 cm. apart.

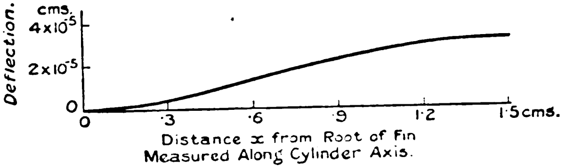


Fig. 20.—Hoop Stress in Fin.

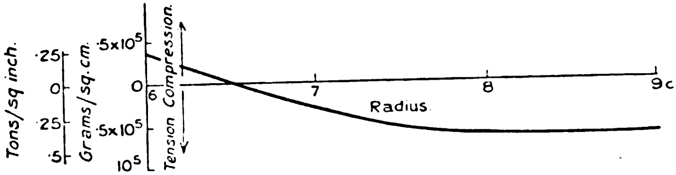
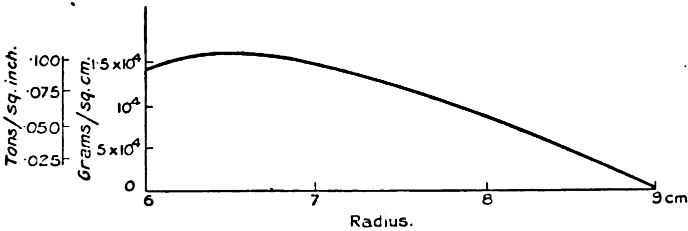


Fig. 21.—Radial Stress in Fin.



number of fins of constant thickness whose dimensions and temperature distributions are the same as those of the fin considered in figs. 3–6. The barrel and the roots of the fins are maintained at a steady temperature of 400° C., and the internal pressure is zero. Fig. 14 shows how the pressure between the cylinder barrel and the root of the fin is determined by the intersection of two pressure-deflexion curves—one for the root of the fin and the other for the barrel. The pressure is found to be about 1/10 ton per sq. inch. Fig. 15 indicates the rapidity with which the deflexion of the barrel at points midway between the fins increases as the distance between the fins increases. This illustrates the importance of spacing the fins closely if an even surface in the cylinder is to result. At the same time it must be remembered that closely spaced fins cause comparatively high circumferential stresses in the barrel, as is clearly demonstrated by fig. 16. Professor Gilbert Cook has shown that under certain circumstances the deflexion of the barrel may exceed the deflexion of the barrel without fins, the condition being $\frac{3\pi}{4n} < x < \frac{7\pi}{4n}$. In the example under consideration this gives values of x lying between 3·18 cm. and 7·41 cm., distances which are too large to occur in normal practice. In any event, the extra deflexion to be expected is not more than 5 per cent. Figs. 17–19 show the deflexions of the barrel relative to the roots of the fins when the fins are 1, 2, and 3 cm. apart respectively. The forms which the barrel assumes are similar but of widely differing magnitudes, the deflexion scales being 100 : 10 : 1. These forms closely resemble those which occur when a barrel of uniform temperature reinforced by external flanges is subjected to internal pressure *, although there is an important change in the stress distribution. For the hot barrel the circumferential stresses are compressive, and decrease as the distance from a fin increases; while in the other case the reverse ensues, the circumferential stresses, which are tensile, being at a maximum at points midway between the fins. And further, increase in the distance between consecutive fins in the former case decreases the circumferential stress, and in the latter increases it. Finally, figs. 20 and 21 indicate the stresses in the fins.

---

* Professor Gilbert Cook, *loc. cit.* p. 304.

XXXVIII. *The Photoelectric Emission from Platinum as Influenced by Heating.* By LARS A. WELO, *Ph.D.*[*]

THIS paper is intended to be in the nature of a reply to a recent one of Kurt Herrmann[†] in *Annalen der Physik* on "The Influence of Gas Content on the Photoelectric Emission and the Electrical Conductivity of Platinum." He comes, naturally, to the very controversial question as to whether or not the photoelectric effect for this metal vanishes on the complete elimination of the occluded gases. My[‡] own experiments of 1922, from which I concluded that platinum remains sensitive photoelectrically, are justly criticised on the ground that the temperatures I used were not sufficiently high to secure even moderate elimination of the gases. These experiments of mine were repeated as long ago as February to May, 1923, and it became apparent at once that the photoelectric sensitiveness of platinum becomes gradually less as the temperature at which platinum is heated is increased. Herrmann and I are now, therefore, in complete agreement on this question as far as the experimental facts are concerned. I do not purpose to discuss the meaning of this result beyond presenting rather rough preliminary data on the effect of scraping, which may be interpreted as an indication that surface impurities are developed during the heating.

The results to be presented will show that the ease with which platinum may be made relatively insensitive towards ultra-violet light is very markedly dependent on the sample of platinum employed. My experiments of 1922 were made on a foil which retained its maximum sensitiveness after heating for many hours at a temperature of 1300° C. In the experiments reported on here, a foil was employed which decreased in sensitiveness to about 1/12 of a previous maximum after having been heated to slightly more than 1400° C. Data are presented for another foil which decreased in sensitiveness to 1/37 of a previous maximum value on heating to only 1140° C.

The possible influence of mercury vapour will also be taken up. Herrmann considers that a certain minimum which appears in a curve showing the photoelectric sensitiveness as a function of the heating current sent through the foil is due to the presence of mercury vapour. It will be pointed out that this minimum disappears as the heating is continued or if the temperature is raised, in spite of the continued presence of mercury vapour. It will also be shown that this minimum appears when somewhat similar experiments are performed in the open air and under conditions such that no mercury vapour can possibly be present. Finally, a few curves are included which show that the effect of adding gases after outgassing by heating is dependent on the particular sample of platinum in use.

---

[*] Communicated by the Author.

[†] Herrmann, *Ann. der Phys.* lxxvii. p. 503 (1925).

[‡] Welo, Phil. Mag. xlv. p. 593 (1923).

The Experimental Procedure and the Apparatus.

The experiments were conducted in the same manner as before. The foil was heated with various increasing heating currents, and the photoelectric current was measured after the metal had become cool. After the first "run" on a new specimen, a run was made with successively decreasing heating currents. This is indicated by the arrows on the figures. Two minutes instead of ten was adopted as the standard time of heating with a given heating current during a run.

The tube was similar to that shown in fig. 2 of my previous paper *. Its diameter was half again as great. It had two side tubes instead of one. The second side tube made possible the determination of the temperatures with an optical pyrometer which had been previously calibrated so as to give the true temperature of platinum. The cylindrical receiving electrode of sheet nickel was placed vertically within the main part of the tube so as completely to surround the foil. Two narrow slits were cut on opposite sides of this electrode, which was placed so that the slits were in line with the side tubes. The parts of the tube near the foil were always baked, while pumping, at 350° C. for two or three hours before making the first run on a new foil. When heating-currents were sent through the foil the pressures increased to as much as 5×10^{-5} mm. of mercury, but when the foil was not being heated the pressure while pumping was constantly of the order 10^{-6} mm., as measured with a McLeod gauge in connexion with the tube through a liquid-air trap. Liquid air was applied to this trap before inserting the foil and sealing up, and was kept in place continually until the work with that foil was complete. As the work on a foil extended over a long time (35 days in one case) the pump was not run all the time. Over-night the pressures sometimes rose to 9×10^{-5} mm., but usually this over-night increase was to 2×10^{-6} mm. The lines near 254 $\mu\mu$ from a quartz mercury arc were used exclusively for the work reported upon. The foils were 13 cm. long, 0·5 cm. wide, and 0·001 cm. thick.

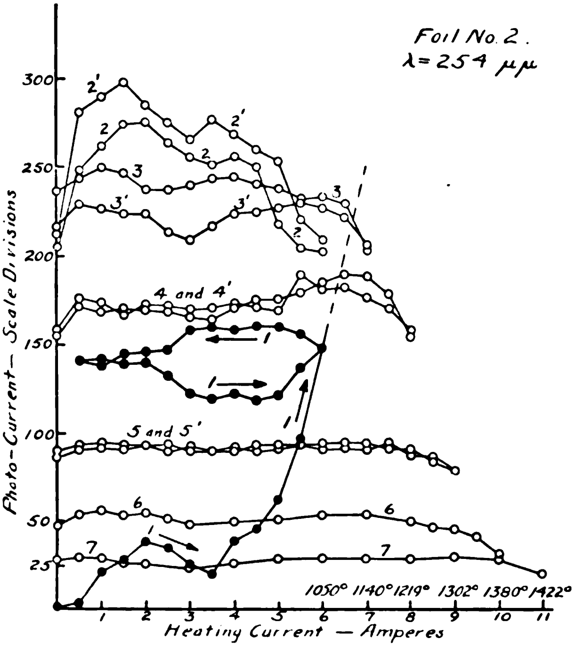
---

* *Loc. cit.*

The Decrease of Sensitiveness on Heating at High Temperatures.

Fig. 1 shows the results obtained with Foil No. 2, the complete history of the foil during the experimental work being given in the caption accompanying the figure. To this history as given in the caption it is only necessary to add that between runs 1 and 2 when the foil was being heated with 6 amperes, T=1050° C., the heating-current

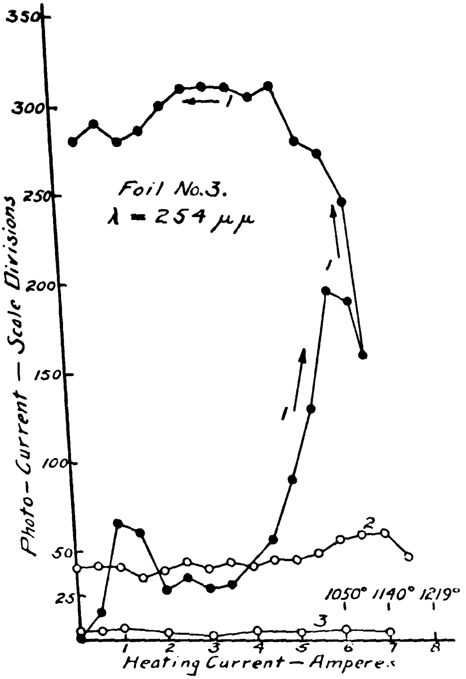
Fig. 1.



1. Original runs on new foil.
2. Immediately after total heating of 110 minutes with 6 amperes, 1050° C.
2'. „ „ „ 240 „ „ 6 „ 1050° C.
3. „ „ „ 60 „ „ 7 „ 1140° C.
3'. „ „ „ 480 „ „ 7 „ 1140° C.
4. „ „ „ 60 „ „ 8 „ 1219° C.
4'. „ „ „ 180 „ „ 8 „ 1219° C.
5. „ „ „ 60 „ „ 9 „ 1302° C.
5'. „ „ „ 120 „ „ 9 „ 1302° C.
6. „ „ „ 80 „ „ 10 „ 1380° C.
7. „ „ „ 40 „ „ 11 „ 1422° C.

was accidentally raised to nearly 7 amperes, T=1140° C., for about three minutes. It is assumed that the greater sensitiveness throughout run 2 as compared with the maximum of run 1 is due to this cause. It is on this assumption that the first part of run 1 is extrapolated along the broken line. In this section of this paper, no data are shown for Foil No. 1 as it was used in the preliminary work of adjusting the electrometer sensibility, slit-width, high resistance, &c. to convenient values. The general behaviour was the same as with Foil No. 2. After having been heated for 150 minutes at a temperature of 1416° C., its sensitiveness was still 1/13 of the previous maximum value.

Fig. 2.



1. Original runs on new foil.
2. Immediately after total heating of 180 minutes with 6 amperes, 1050° C.
3. „ „ „ 60 „ „ 7 „ 1140° C.

Foil No. 3, which came from the same supply as Foils Nos. 1 and 2, proved to be strikingly different in its behaviour. This foil, too, became less sensitive to $\lambda=254\ \mu\mu$, but this insensitive condition could be brought about much more easily. This is shown in fig. 2. After heating to only 1140° C., the sensitiveness was reduced to 1/37 of a previous high value. I do not recall nor do my notes indicate any conditions different from those existing when Foil No. 2 was being studied. The pressures were about 10^{-6} while pumping, and the over-night increase was to 8×10^{-5}, which is slightly less than that observed with Foil No. 2 during the early part of the work with that foil.

It is clear from these results that I cannot now maintain my previous conclusion that the photoelectric effect does not tend towards zero if platinum is heated in a vacuum of the order of 10^{-6} mm. of mercury at sufficiently high temperatures. On this point, as an experimental fact, I am in complete agreement with Herrmann and the other workers of the Hallwachs-Wiedemann group. I am likewise in accord with Tucker * and Woodruff †, who have conducted similar work in this country. The results shown in figs. 1 and 2 explain much of the disagreement which has existed in this field. For example, in my previous work I heated at 1300° C. and observed no tendency for the photoelectric current to become smaller. I did not go beyond 1300° C. because evaporation of platinum becomes marked there, and evaporation is to be avoided if one wishes to heat for a long time. In the present experiments, heating at 1300° C. decreased the sensitiveness to about a third, as shown in runs 5 and 5′ of fig. 1. With still another foil, No. 3 of fig. 2, the effect had fallen to 1/37 on heating to only 1140° C. Small amounts of impurities of an unknown nature undoubtedly play an important part in the results obtained.

Scraping to remove possible Surface Impurities.

It is perfectly natural to attribute the smaller photoelectric sensitiveness of platinum after heating at high temperatures to the smaller concentration of occluded gases, in view of the fact that gases are continually being driven off during the heating. This has been the usual explanation. It is not in complete accord with the manner in which photoelectric sensitiveness is recovered, as has recently been pointed out by Woodruff ‡. Nor is it in accord with the appearance of a relatively insensitive condition when one heats platinum in the region of 100° to 500°, as has been observed by Herrmann * and myself † when the heating is done in a vacuum, and by Zeleny ‡ and Davidson § when the experiment is conducted out in the open at atmospheric pressure. It is hard to avoid a suspicion that some insensitive surface condition is built up during the heating, in spite of the best vacuum conditions and careful choice and preliminary handling of the platinum. There is wide room for speculation as to the structure of this insensitive layer. It was with the possibility in mind that the surface might be chemically different from the body of the platinum, that I undertook to scrape the metal after it had been made nearly insensitive towards radiation of wave-length $\lambda=254\ \mu\mu$. The tests were made on Foil No. 3 directly after taking run 3 of fig. 2. The runs shown in fig. 3 are consecutive.

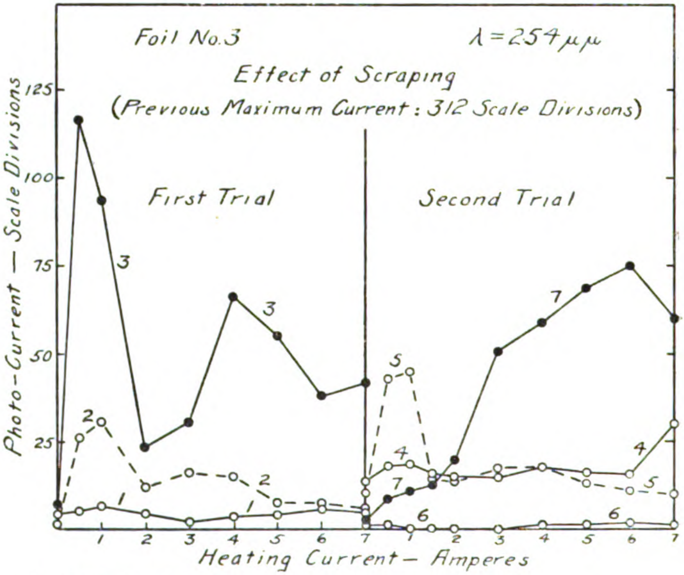
---

* Tucker, Phys. Rev. xxii. p. 574 (1923).

† Woodruff, Phys. Rev. xxvi. p. 655 (1925).

‡ *Loc. cit.*

Fig. 3.



1. Same as run 3, fig. 2.
2. Immediately after standing in air 1 hour.
3. ,, ,, scraping.
4. ,, ,, heating 60 minutes with 7 amperes, 1140° C.
5. ,, ,, standing in air 1 hour.
6. ,, ,, heating 120 minutes with 7 amperes, 1140° C.
7. ,, ,, scraping.

---

* *Loc. cit.* † *Loc. cit.*

‡ Zeleny, Phys. Rev. xii. p. 321 (1901).

§ Davidson, Phys. Rev. xxvi. p. 1 (1908).

It was necessary to make a comparison with the effect of mere exposure to air, since the scraping had to be done out in the open. To remove the foil, scrape, replace and re-exhaust took about an hour, so that previous to the comparison runs the foil was exposed to air for about the same length of time. Runs 3 and 7 were made after scraping. These experiments are admittedly rough, and the results are not concordant between themselves. But it is significant that after scraping the foil is, on the whole, more sensitive than after mere exposure to air.

This scraping experiment should be done in such a way that the metal could be scraped, filed, or polished immediately after a low sensitiveness had been attained by heating, without removing from the tube or destroying the vacuum. At the time of this work it seemed to be too difficult from a mechanical standpoint. It seems now, however, that it should be less difficult if the platinum were used in the form of a wire rather than in the form of foil. It should be possible to draw a wire-drawing die or a sort of hollow, closely fitting file along the wire after it has been made relatively insensitive, remove the old surface, and form a new one of nearly gas-free platinum.

Does Mercury Vapour cause Low Sensitiveness when Heatiny at 100° *to* 500° *C.?*

When the photoelectric current from platinum is measured after heating at various increasing temperatures, one finds lower values in the interval of 100° C. to 500° C. Reference is made to figs. 3 and 4 of my previous paper[*]. The existence of this minimum has been confirmed by Herrmann[†], who also noted its great persistence. The reader should note fig. 7 of his paper. He undertook to trace its origin, and concluded that it is very probably due to mercury vapour from the pumps. This conclusion is strongly supported by the curves 2, 3, and 5 of his fig. 8, these curves being obtained after the liquid air was removed from the trap, whereas all of the other curves which did not show the minimum were obtained when mercury vapour should be absent.

There are two circumstances, however, which must be considered before this explanation can be accepted. One is the fact that this minimum disappears when a run is made after the platinum has been heated for a sufficiently long time at a high enough temperature even if mercury vapour is permitted to be present. This is shown in fig. 5 of my previous paper[*], and is also shown by Herrmann himself. Curve *d* of his fig. 7 is perfectly straight and horizontal, and he emphasizes the fact that no liquid air was used in all of his work shown in fig. 7.

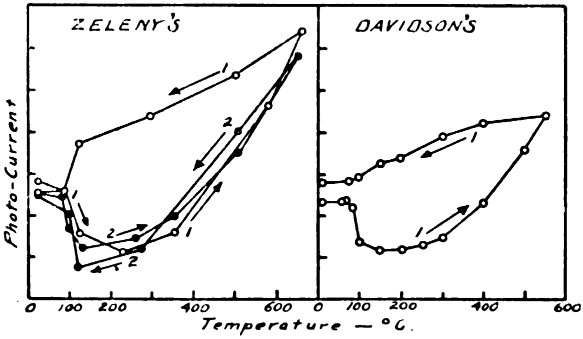
---

[*] *Loc. cit.*

[†] *Loc. cit.*

The other circumstance is that this minimum appears in some early photoelectric experiments on platinum by Zeleny[†] and Davidson[‡]. Their results are reproduced in fig. 4, the curves of Davidson being somewhat distorted as to scale. Their procedure was different from Herrmann's and from mine in that the photoelectric current was measured while the metal was hot. The significant thing for us, however, is that the experiments were conducted out in the open at atmospheric pressure and with apparatus which did not involve the presence of mercury. The only enclosures employed were those necessary for electrostatic shielding. It is clear then that the minima of the curves showing photoelectric sensitiveness as a function of heating-current or temperature of heating cannot be accounted for in the simple manner proposed by Herrmann. They disappear on long-continued high-temperature heating in spite of the presence of mercury vapour, and they are found with slightly used foils even when mercury vapour must be considered to be entirely absent.

Fig. 4.



Photoelectric current from platinum as function of temperature when heated in air at atmospheric pressure.

---

[*] *Loc. cit.*

[†] *Loc. cit.*

[‡] *Loc. cit.*

Some Experiments on the Influence of Gases.

After the sensitiveness of Foils Nos. 1 and 2 had been reduced to relatively low values, some experiments were made to test the influence of gases. Similar work was done with Foil No. 3 after the effect of scraping had been looked into. The results for all three foils are given in fig. 5. The runs are all consecutive, and the immediate previous treatments are described in the caption. It should be remembered that the previous maximum photoelectric current with Foil No. 2 was 299 scale-divisions, with Foil No. 3 it was 312 scale-divisions, and with Foil No. 1 it was over 400 scale-divisions. It is seen that in no case did treatment with gas fully restore the platinum to its previous maximum sensitiveness. It is noticed, too, that Foils Nos. 1 and 2 underwent no change after standing in a high vacuum, in hydrogen, in oxygen, or in the "condensable" gas. By condensable gas is meant that portion of the gas removed from the foil, or the surrounding parts of the tube, by heating, which had condensed in the liquid-air trap. It was released by removing the liquid-air. Foil No. 3 behaved differently. This foil regained sensitiveness on mere exposure to air or to the residual gases of low pressure within the tube. In one case this recovery was to nearly one-half of the previous maximum of 312 scale-divisions. The results of this section bring out again the influence of the particular sample of platinum on the results obtained in photoelectric work. Foils Nos. 1 and 2, which had been reduced in sensitiveness only with great difficulty, showed no tendency to recover on coming in contact with gases. Foil No. 3, however, which had been made insensitive very easily, recovered from a quarter to nearly half of its previous high sensitiveness on standing in air or in a high vacuum.

Heating the photoelectrically insensitive platinum to bright yellow glow in hydrogen, in oxygen, or in condensable gas changes its behaviour when it is subsequently carried through a series of increasing temperatures. The two runs made with Foil No. 2 after heating in condensable gas are in general agreement between themselves, as are also those made after heating the foil in hydrogen. These results of heating with hydrogen are in agreement with those of Herrmann [*] in that the maximum appears at the higher temperatures. It is not known whether or not this maximum sensitiveness could have been made to approach the previous

---

[*] *Loc. cit.*

Fig. 5.

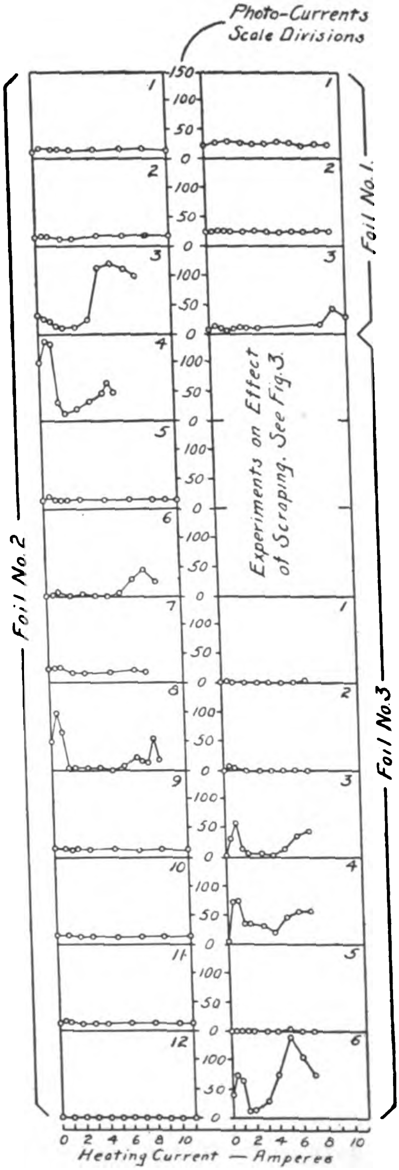


Photo-Currents
Scale Divisions
150
100
50
0
1
2
3
4
5
6
7
8
9
10
11
12
Foil No. 1.
Experiments on Effect of Scraping. See Fig. 3.
Foil No. 2
Foil No. 3
0 2 4 6 8 10
0 2 4 6 8 10
Heating Current — Amperes

Foil No. 2.—1. After standing in high vacuum 3 days following run No. 7, fig. 1.
2. „ standing in condensable gas 14 hours, pressure=2 mm.
3. ,, heating in condensable gas, pressure=2 mm.
4. Immediately after preceding run.
5. After heating 70 minutes with 11 amperes, 1422° C.
6. „ ,, in hydrogen, pressure=3 mm.
7. Immediately after preceding run.
8. After heating in condensable gas, pressure=1·5 mm.
9. Immediately after preceding run.
10. After heating 30 minutes with 10 amperes, 1380° C.
11. ,, standing in oxygen 45 hours, pressure=10 cm.
12. „ heating in oxygen, pressure=3 mm.

Foil No. 1.—1. After heating 90 minutes with 11 amperes, 1416° C.
2. ,, standing in hydrogen 48 hours, pressure=14 cm.
3. „ heating in hydrogen, pressure=12 cm.

Foil No. 3.—1. After heating 120 minutes with 7 amperes, 1140° C.
2. ,, standing in air 2 hours, atmospheric pressure.
3. ,, ,, ,, 8 days, ,, ,,
4. ,, ,, in vacuum 1 day, then in air 4 days.
5. ,, heating 105 minutes with 7 amperes, 1140° C.
6. ,, standing in high vacuum 4 days.

maximum sensitiveness by choosing other pressures or other temperatures or times of heating. The results of heating in oxygen are also in agreement with Herrmann's results. After heating in this gas the sensitiveness remains low at all heating currents.

This experimental work was done during the spring of 1923 at the University of Wisconsin. I am indebted to Professor C. E. Mendenhall for the opportunity to do it and for valuable suggestions and criticism.

The Rockefeller Institute for Medical Research,
New York City, March 5, 1926.

XXXIX. *The Transference of Energy in Collisions between Electrons and Molecules.* By J. S. TOWNSEND, *M.A., F.R.S., Wykeham Professor of Physics, Oxford,* and C. M. FOCKEN, *B.Sc., Lincoln College, Oxford**.

1. THE well-known electrical properties of gases which are observed in experiments on currents between two electrodes where potentials less than one hundred volts are used, have been the subject of many investigations, and suggestions have recently been made to account for the increase in conductivity with the force on certain hypotheses relating to the transference of energy from electrons to molecules which are said to be required by the quantum theory.

In these explanations of the conductivity no attempt is made to account for many of the principal features of the phenomena, and there is disagreement on many points with the results of the experiments.

It is of interest therefore to examine the experimental evidence which is usually quoted in support of the laws that have been adopted with regard to the transference of energy in quanta from electrons to molecules. This evidence seems to be very defective, and if the inquiry be extended to other experiments on the motion of electrons in gases at low pressures, the theory of the transfer of energy in quanta as it is generally stated is found to be quite untenable.

As the theory relates to a large extent to collisions in which electrons lose energy in amounts corresponding to resonance potentials, and large photo-electric effects which are supposed to result from the radiation from molecules, we have recently made some experiments with neon and helium in order to determine the relative importance of the photo-electric effect and the effect of ionization by collision in contributing to the conductivity of these gases. The results are the same as those which we obtained by other methods, but in the recent experiments a simpler form of apparatus was used which gives a more direct method of comparing the increases in conductivity resulting from these two processes.

2. The hypotheses relating to the transference of energy in quanta are described by Jeans † in his report on the quantum theory. In this report it is stated that the general

---

* Communicated by the Authors.

† J. H. Jeans, 'Report on Radiation and the Quantum Theory,' second edition, 1924.

truth of the ideas relating to the transference of energy from electrons to molecules is confirmed by experiments made by Franck and Hertz, and some of the results which were obtained with mercury vapour are quoted as examples of what may be expected to occur in general. The application of the quantum theory to the conductivity of gases is more fully described by Bloch *, and in his book on the subject special consideration is given to experiments exhibiting discontinuities in currents due to electrons moving under accelerating potentials. The principal hypotheses which have been adopted are the following :—

Electrons moving with small velocities rebound without any loss of energy whatever from atoms with which they collide,

As the velocity of the electron is increased a point is reached where the electron loses all its energy in a collision.

The only amounts of energy which an electron may lose in a collision are the precise amounts corresponding to resonance potentials or the ionizing potential.

These hypotheses, it will be noticed, are not in agreement with the principle of the conservation of momentum. The resonance potentials are comparatively large, being of the order of 10 volts, so that in many experiments the energy of each electron is less than that corresponding to a resonance potential of the gas. In these cases, if a molecule be supposed to be at rest before a collision, it is also at rest after the collision if the electron loses no energy, but the momentum of the system is changed owing to the change in the direction of motion of the electron.

3. With regard to the first hypothesis it may be stated that there are several experiments which show that electrons lose only a small proportion of their energy in collisions with molecules, but there are no experiments which show that the loss of energy is absolutely negligible in collisions where the direction of motion of the electrons is changed.

There are experiments which show that electrons lose some energy in these collisions, when the kinetic energy is large compared with the energy of agitation of the molecules. Collisions also do occur in which the electrons move almost exactly in the same direction before and after a collision, and in these cases the loss of energy is negligible in comparison with the loss in collisions where electrons are deflected. In

---

* L. Bloch, 'Ionization et resonance des Gaz et des Vapeurs,' 1925.

the following discussion we shall consider only the collisions in which the direction of motion of the electrons is changed.

The idea that electrons lose no energy in collisions with atoms is supposed to have been established by Franck and Hertz [*], from measurements of velocities of electrons before and after collisions with molecules. A little consideration shows that the exact amount of energy which is lost in collisions cannot be found by this method. The difficulties enumerated by Bloch which occur in the determinations of critical potentials occur also in the measurements of the velocities before and after collisions. In helium, for example, a series of resonance potentials, V_1, V_2, etc. were obtained by Franck and Knipping [†], which were considered to be in agreement with the formula $eV = k\nu$ giving the resonance potentials in terms of the frequencies ν of the spectral lines. The wave-lengths of these lines were subsequently determined by Lyman [‡], but the results he obtained were not in good agreement with the resonance potentials as found by Franck and Knipping. This discrepancy has shown that in estimating the correction for contact potential and the distribution of the velocities of the electrons an error amounting to 0·7 volt may occur in the absolute values of the resonance potentials. It seems very improbable that velocities can be measured by this method to an accuracy of one-tenth of a volt. The experiments with the smaller velocities may possibly be interpreted as showing that an electron does not lose more than about one per cent. of its energy in collisions with molecules, but they do not show that the loss of energy in a collision is absolutely negligible.

4. It may also be pointed out that another source of error may arise in the experiments on the loss of energy in collisions described by Bloch [§], as the electric force is not zero in a gas contained in a metallic vessel when a stream of electrons from a filament is projected through a grid into the vessel. The space inside the vessel becomes negatively charged and there is a force towards the surface tending to increase the velocity of electrons which may move out through an aperture in the boundary. When a space with an equipotential boundary contains a gas at low pressure the space charge depends on the dimensions of the vessel

---

[*] J. Franck and G. Hertz, *Verh. d.D. Phys. Ges.* xvi. pp. 457, 512 (1914).

[†] J. Franck and P. Knipping, *Zeit. f. Phys.* i. p. 320 (1920).

[‡] T. Lyman, 'Nature,' vol. cx. p. 278 (1922).

[§] L. Bloch, *loc. cit.* p. 32.

and the intensity of the stream that enters it. This type of apparatus is used in several experiments, but the intensity of the stream of electrons which enters the space is not mentioned. As the smaller subsidiary currents are measured by a galvanometer the original filament emission would appear to be several microamperes. The following rough calculation indicates the order of the force which would be developed due to accumulation of charge in a vessel of ordinary dimensions if the rate at which the electrons reach the boundary were due to diffusion alone. In order to find the average time during which an electron may move about inside the vessel without touching the boundary, we may take the case of an electron at a point P at a mean distance of two centimetres from the boundary moving with a kinetic energy corresponding to three volts in helium at 2 millimetres pressure. If there be no loss of energy in collisions the kinetic energy remains constant, the velocity of the electron being 10^8 cm. per sec. The mean free path of the electron corresponding to this velocity is ·025 cm., so that the rate of change of the mean square of the distance R of the electron from the point P is obtained from the formula : $dR^2/dt = 5 \times 10^6$. Thus the time required for the electron to reach the boundary is on an average 8×10^{-7} second. If a current of 10^{-5} ampere entered the space the total charge in the space at any instant would be $2{\cdot}4 \times 10^{-2}$ electrostatic unit, and if the boundary were a sphere of 2 centimetres radius the force at the surface would be 1·8 volts per centimetre.

If the electrons lose energy in collision with molecules, their velocity of agitation would be reduced, and there would be a corresponding increase in the force at the boundary. A considerable error may thus be made in treating the space inside a metal enclosure as a "force free" space, and in drawing conclusions from measurements of currents emerging from an aperture it is desirable to take into consideration the force due to the space charge.

5. The hypotheses relating to transference of energy in exact amounts involve other difficulties. They imply that the number of collisions in which electrons lose energy in amounts corresponding to resonance potentials is greater than the number of collisions in which molecules are ionized under some conditions where large increases of current due to ionization by collision are obtained. The question arises as to the probability of an electron losing an amount of energy equal to eV_1, when its energy before the collision exceeds that amount : V_1 being a resonance potential.

The evidence on this point as obtained from experiments on mercury vapour, is very uncertain, and the results obtained by different observers are not in good agreement.

In an investigation by Franck and Einsporn[*], on currents depending on the accelerating potential applied to electrons, there are fourteen points of discontinuity, in the curve representing the currents, obtained by changing the accelerating potential from 4 to 9 volts, giving fourteen resonance potentials between these two points. The curves seem to indicate that the probability of an electron losing energy in any of the critical amounts is small and is of the same order for each of the fourteen resonance potentials, but under these conditions sharp discontinuities in the current would not be expected.

Also, owing to the distribution of the velocities of the electrons emitted from the filament and the effect of the retarding field due to the space charge, the electrons collide with different velocities, so that even if there were critical amounts of energy characteristic of the molecules of the gas, abrupt changes in currents would not occur when the accelerating potential passes through these points.

A different result has been obtained by Foote and Mohler[†], who found two critical potentials between 4 volts and 9 volts, which seems to indicate that electrons lose energy in a large proportion of collisions when they collide with molecules of mercury vapour with velocities corresponding to two of the critical potentials observed by Franck and Einsporn.

The theory has also been tested by investigations of another kind, where observations are made of the photo-electric effect due to the radiation emitted by molecules after absorbing energy in amounts equal to the quantities eV_1, eV_2, etc. In the experiments on this principle made by Richardson and Bazzoni[‡], a current from a filament was sent through mercury vapour, but no photo-electric effect was observed when the accelerating potential was less than 10·5 volts; also the photo-electric effect with larger accelerating potentials was very small compared with the current from the filament. This result is in accordance with those we have obtained from experiments with helium and neon, which showed that the photo-electric effect must be extremely small in comparison with the effect of ionization by collision.

---

[*] J. Franck and E. Einsporn, *Zeit. f. Phys.* ii. p. 18 (1920).

[†] P. D. Foote and F. L. Mohler, 'Origin of Spectra,' 1922.

[‡] O. W. Richardson and C. B. Bazzoni, Phil. Mag. [6] xxxii. p. 437 (1916).

6. The transference of energy from electrons to molecules may be determined by a different method from the results of experiments on the motion of electrons in a uniform electric field.

In the initial stages of the motion of electrons which start with a small velocity, the kinetic energy of the electrons increases as they move in the direction of the electric force; and since the direction of motion is changed in the collisions with molecules of the gas, the kinetic energy of the electrons appears as energy of agitation. After moving some distance in the direction of the force a steady state of motion is attained where the electrons lose energy in collisions with molecules at the rate at which they acquire energy by moving in the direction of the force. At this stage the motion of the electrons is represented by a mean velocity of agitation U and a mean velocity W in the direction of the force.

If it be supposed that the electrons lose no energy in collisions with molecules, until they attain the energy corresponding to the first resonance potential V_1, and then lose all their energy, they would again acquire the energy eV_1 after moving a further distance $z=V_1/Z$ in the direction of the force (Z). Thus the average energy of agitation of an electron when expressed in volts would be a certain fraction of the potential V_1. If AV_1 be the average energy, the coefficient A is independent of the electric force and pressure provided that the pressure is sufficiently great to ensure that each electron makes several collisions with molecules while its energy is slightly above the critical value V_1. The factor A depends on the velocity of an electron in the direction of the force during the time its energy of agitation rises from zero to V_1: the value of A may thus be seen to exceed ·5, but for the purpose of this calculation this value may be attributed to A.

Under these conditions, if the first resonance potential in helium be taken to be 20 volts, the mean energy of agitation of electrons in the steady state of motion would be about 10 volts for any value of the electric force and any pressure of the gas. As no result of this kind has been obtained in the experiments on the determination of the values of U, it cannot be maintained that the electrons lose no energy except in amounts equal to eV_1.

7. The velocity of agitation U and the velocity W in the direction of the electric force have been determined for several gases over a wide range of electric force Z and gas

pressures p in the Electrical Laboratory, Oxford [*]. In all cases the velocities U and W were found to depend on the ratio of the electric force Z to the gas pressure p.

The energy of agitation may be expressed as the product of the atomic charge and a potential, and this potential may be taken as representing the kinetic energy of an electron moving with a velocity U.

In helium at 20 millimetres pressure the potential which represents the energy of agitation is ·42 volt when the electric force Z is 4 volts per centimetre. The energy of agitation increases when the pressure is reduced or the force increased. At 8 millimetres pressure the potential which represents the energy of agitation is 1 volt, with the same electric force of 4 volts per centimetre.

Thus not only is there a large change in the mean energy of agitation with the pressure, but also this energy is very much less than the energy corresponding to 10 volts.

8. The fact that the energy of agitation of electrons, moving under a small electric force, exceeds the energy of agitation of the molecules of the gas (which is approximately ·037 volt at 15° C.) shows that the electrons lose only a small proportion of their energy in collisions with molecules, as was pointed out when the first experiments [†] on the energy of agitation of electrons in air were made several years ago.

In order to determine the exact amount of energy lost in collisions it is necessary to find the velocity W in the direction of the electric force for the same forces and pressures as those used in finding the velocity of agitation. The proportion λ of the energy of an electron which is lost in a collision is thus obtained from the formula

$$\lambda = 2{\cdot}46 \times W^2/U^2.$$

For the range of values of the energy of agitation (from ·43 volt to 3·4 volts) the value of λ is approximately constant, and equal to $2{\cdot}5 \times 10^{-4}$ in helium.

Hence, even when the electrons lose only a very small proportion of their energies in collisions, this loss is sufficient to control the energy of agitation. This is due to the fact that the number of collisions per centimetre in the direction of the electric force (equal to U/Wl, where l is the mean free path) is large since U is large compared with W.

---

[*] The results of the principal experiments, and tables of the velocities U and W are given in the pamphlet "Motion of Electrons in Gases," Clarendon Press, Oxford, 1925.

[†] Proc. Roy. Soc. A., lxxxi. p. 484 (1908).

As the electric force is increased values of the ratio Z/p are attained at which the effect of ionization by collision becomes appreciable, and for these values of the ratio Z/p there is a marked increase in λ. In the ordinary notation adopted to represent the rate of increase of currents due to ionization by collision the values of α/p are approximately ·04 and ·12 for the values of Z/p, 3 and 5 respectively, and the corresponding values of λ are $4{\cdot}15 \times 10^{-4}$ and $9{\cdot}8 \times 10^{-4}$.

It is important to notice that the change from the small values of λ, $2{\cdot}5 \times 10^{-4}$, to the large values as the force increases, is accompanied by the appearance of additional electrons due to ionization by collision. If there were large losses of energy in amounts corresponding to resonance potentials which are smaller than the ionization potentials, increases in the value of λ would have been observed before ionization by collision became appreciable, and no effect of ionization by collision would have been observed with values of Z/p as small as 3 or 5.

It may be mentioned that the energy required to ionize a molecule cannot be obtained from the rate of increase of λ with the force by simple calculation. When new electrons are generated in the gas the quantity $2{\cdot}46W^2/U^2$ does not accurately represent the average loss of energy of an electron in a collision. When an electron loses a large proportion of its energy the value of U is reduced, but if in addition a new electron is set free from a molecule with a small initial energy of agitation, a further reduction in the average value of U occurs owing to the increase in the number of electrons with small kinetic energy. In consequence of these two effects there is a large increase in the ratio W^2/U^2 when ionization becomes appreciable.

9. Bloch suggests that the conclusions which have been drawn from these experiments with regard to the values of λ and variations of the mean free path L are unreliable, since the formulæ connecting λ and L with the velocities U and W which are used are obtained on the classical principles of mechanics, and large losses of energy in amounts corresponding to resonance potentials are not considered.

As the experiments do not lead to any conclusion which is contrary to the principles involved in determining these formulæ, and as the values of the energy of agitation found experimentally are completely different from the value indicated by the theory of transference of energy in quanta, it would be unreasonable to adopt the latter theory.

In the kinetic theory of gases in its classical form as applied to the motion of electrons in gases, it is not necessary to assume that the mean free path or the mobility is constant. In fact, if the mean free path of an electron be supposed to be constant, the mobility must change with the electric force. The formula connecting the velocity W in the direction of the electric force with the mean free path may be written

$$W=\frac{Z}{p}\times\frac{eL}{mU}\times{\cdot}815,$$

where p is the gas pressure, and L the mean free path at 1 millimetre pressure.

In this case, where the electrons move under a uniform electric force, the only difficulty in obtaining the formula occurs in determining the distribution of the velocities about the mean, as the numerical constant depends on this distribution. But the constants found by assuming different distributions are not much different from the value ·815, which is the number obtained on the hypothesis that the velocities are distributed according to Maxwell's law. Whatever be the correct value of the numerical constant, the mobility, which is proportional to $\frac{e}{m}\times\frac{L}{U}$, must diminish as U increases. Thus, as the theory requires that U should increase with the ratio Z/p, it also requires that the mobility should diminish as Z/p increases.

10. The velocities W as found experimentally confirm this conclusion in so far as it has been found that W does not increase directly as the electric force or inversely as the gas pressure.

The quantity $W.U.p/Z$ is not constant, which shows that the mean free path varies with the velocity of agitation. When this result was first obtained * in the experiments on the motion of electrons in air, it was pointed out that collisions between electrons and molecules cannot be supposed to be analogous to collisions between elastic spheres. This analogy implies that in a collision with a molecule at rest the deflexion of an electron is independent of the velocity of the electron. Also, with spheres, the mean free path is a constant independent of the velocity of the electron, as it

---

* J. S. Townsend and H. T. Tizard, Proc. Roy. Soc. A. vol. lxxxviii. (1913).

represents the average distance traversed by an electron between two consecutive contacts with spheres of fixed radii.

In the formula for W the shape of the molecules is not considered, the length L being defined as the average distance an electron moves in a given direction with the velocity U before all directions of motion become equally probable, when the electric force Z is zero. In all cases the length L changes with the velocity of agitation, and in most cases, as in air, L increases as U diminishes for a large range of values of U.

11. There are also remarkable discrepancies between the conclusions drawn by German physicists from experiments on the performance of electrons in diatomic gases contained within an equipotential boundary where the space is said to be "force free," and the properties of these gases which may be deduced from the determinations of the motion of electrons in a uniform electric field.

The former experiments have been interpreted as showing that the loss of energy of electrons in collisions with molecules of oxygen is much greater than the loss with molecules of nitrogen or hydrogen, and it has been concluded that molecules of oxygen, and other electronegative gases, are surrounded by an intense electric field extending to a considerable distance which exercises an attractive force on electrons *. The only force of this kind which is recognized in ordinary mechanics is the force due to an electric charge, but as it cannot be supposed that molecules of oxygen in their normal state are positively charged, the above statement implies that there is an attractive force on electrons which constitutes a special property of molecules of oxygen.

If there were any field of force surrounding a molecule of oxygen much stronger than the fields of force surrounding molecules of nitrogen or hydrogen, the mean free paths of electrons would be shorter in oxygen than in these two gases. A comparison of the mean free paths in these gases, as deduced from the values of U and W, shows that it is in hydrogen that the free paths are the shortest.

Usually it is assumed that in the electric field surrounding a molecule the force repels electrons in some parts of the field and attracts electrons in other parts, the normal induction through a closed surface surrounding the molecule being zero. The intensity and distribution of the force in this field depends on the number and positions of the

---

* L. Bloch, *loc. cit.* pp. 17, 33.

electrons in the molecule. When the number of electrons is small the force in the external field may be greater than when the number is large.

The values L depend on the velocity U, but for a large range of values of U, from 3×10^7 to $1{\cdot}2\times 10^8$ cm. per sec., the free paths are longer in oxygen than in nitrogen or hydrogen. The following are the mean free paths of electrons moving with a velocity of agitation 6×10^7 cm. per sec., in these gases at one millimetre pressure: in oxygen * L=·057 cm., in nitrogen L=·029 cm., in hydrogen L=·0215 cm.

Thus the longer free paths are obtained in the gases of large atomic weight. It is interesting to observe that a similar result was obtained with monatomic gases. The velocities U and W have been determined for three monatomic gases, and the following are the mean free paths at a millimetre pressure corresponding to the velocity of agitation $U=6\times 10^7$: in argon L=·75 cm., in neon L=·21 cm., in helium L=·048 cm.

The large values of L show that in many collisions with molecules the direction of motion of the electron is very nearly the same before and after the collision, and it is to these collisions that we refer in section 3 in stating that the loss of energy is negligible. In equating the average loss of energy λ to the quantity $2{\cdot}46 \,.\, W^2/U^2$, collisions of this type are left out of consideration and the total number of collisions per second of each electron is taken as U/L.

12. The experiments on the measurements of the velocities U and W show that the motion of electrons through a gas is completely controlled by the losses of energy in small amounts when the electric forces are small, so that when the forces are increased and ionization by collision begins to appear the losses in the smaller amounts cannot be left out of consideration. The simplest experiments on the effect of ionization by collision are those where electrons move between two parallel plates and the currents are measured with different potentials between the electrodes. A supply of electrons may be obtained by the action of ultra-violet light on the negative electrode, or from a filament, which may be situated near the negative electrode or in the plane of the negative electrode and the mean potential of the filament maintained at the same potential as that of the negative electrode.

---

* The value of L for oxygen is taken from Brose's recent experiments with that gas. H. L. Brose, Phil. Mag. i. p. 536, Sept. 1925.

The number of electrons that pass from the negative electrode, or from the filament, to the positive electrode increases with the potential difference between the electrodes, but for certain values of this potential there are large increases in the current between the electrodes which are generally attributed to ionization by collision. Usually the increase of current due to this cause has been found to be so gradual that it is impossible to determine the exact point at which a definite effect of ionization by collision begins to appear, but according to Franck and Hertz * there is an abrupt increase of current in helium when the potential difference between the plates is 20 volts and in neon when the potential difference is 16 volts.

According to the original interpretation of these and other experiments made by Franck and Hertz†, the electrons lose no energy in collisions with molecules of the gas until they attain the energy required to ionize a molecule, and immediately the electrons acquire that amount of energy they ionize the molecules with which they collide. The potentials 20 ‡ volts and 16 volts were therefore said to be the ionizing potentials in these gases.

From our point of view these numbers represent upper limits of the ionizing potentials, as it has been shown that electrons lose some energy in collisions before they acquire sufficient energy to ionize molecules, and there is no reason for supposing that an appreciable proportion of the electrons ionize molecules when they attain the exact amount of energy which represents the work done in separating an electron from a molecule.

13. According to the quantum theory of the transference of energy in its more recent developments, electrons lose energy in collisions with molecules in amounts proportional to the frequency of certain spectral lines. These amounts may be expressed in potentials V by the formula $eV = h\nu$, where e is the atomic charge, h Planck's constant, and ν the frequency of the spectral line.

Thus the resonance potentials V_1, V_2, etc. are found accurately from measurements of spectral lines. · According to the theory the resonance potentials are less than the ionizing potential, so that if a large proportion of the electrons lose energy in amounts corresponding to resonance potentials, the effect of ionization by collision would be very

---

* J. Franck and G. Hertz, *Verh. d. D. Phys. Ges.* xv. p. 929 (1913).

† J. Franck & G. Hertz, *Phys. Zeits.* xvii. p. 430, 1916.

‡ The number 20·5 appears in some tables.

small in many experiments where large increases in current have been found to be due to that process of ionization. It is necessary therefore to suppose that in some gases losses of energy in amounts corresponding to resonance potentials occur only in a very small proportion of the total number of collisions in which the energy of the electron exceeds those amounts.

But the principal difficulty in connexion with the theory is that in some gases the resonance potentials, as determined from the wave-lengths of the spectral lines, are greater than the ionizing potentials which were determined experimentally. From Lyman's recent measurements of wave-lengths * the lowest resonance potential in helium is found to be 20·55 volts and the greatest 24·55 volts, the latter according to the theory being the ionizing potential.

In order to meet these difficulties other experiments were made from which it has been concluded that the ionizing potential in helium is about 25 volts, and the increase in current which occurs at lower potentials is said to be due to a photo-electric effect. Similarly in neon the ionizing potential in that gas is now supposed to be 21·5 volts instead of 16 volts.

If these conclusions be correct, it is remarkable that in Franck's earlier experiments an abrupt increase of current was not observed in helium at the point where the potential difference between the electrodes was 25 volts or in neon at 21·5 volts, especially as it is claimed that critical potentials may be determined by discontinuities in currents even when the gas contains small quantities of impurities.

14. In the original investigations which were made in connexion with the theory of ionization by collision, the conductivity of a gas between parallel plates was examined very carefully, and it was found that the experiments were accurately explained on the hypothesis that the increases in the currents were due to ionization of molecules of the gas by collisions with electrons.

No other process of ionization has since then been suggested which gives a consistent explanation of the principal experiments on the conductivity between parallel plates.

The question arises as to whether any appreciable part of the increases in currents obtained by increasing the potential between the plates may be attributed to a photo-electric effect.

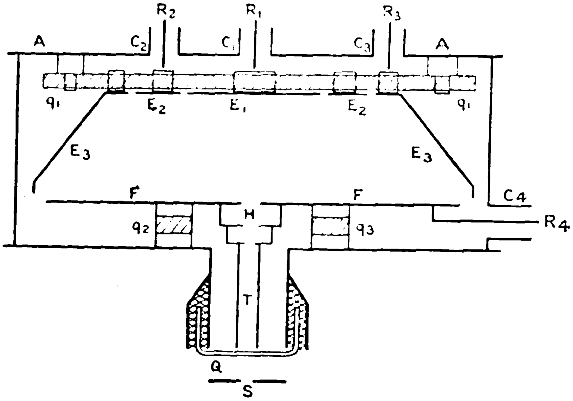
---

* T. Lyman, *loc. cit.*

The experiments which have hitherto been made to detect a photo-electric effect of radiation due to small currents in a gas, have shown that there is no photo-electric effect which is comparable with the effect of ionization by collision. This result was obtained by Gill * in experiments with air in which the initial supply of electrons was obtained by ultra-violet light. A similar result was obtained by a different method for currents in helium †, neon, nitrogen, and hydrogen ‡, where the initial supply of electrons was obtained from a filament in the space between two parallel plates. In these methods of investigation a photo-electric effect would have been indicated by the difference between two currents, so that a small effect comparable with the experimental error in the measurement of a current might have escaped observation.

As the question is of importance from a theoretical point of view, it was considered desirable to make another investigation by a method in which the electrodes are arranged so that a small photo-electric effect would be indicated more directly.

Fig. 1



15. In the investigations which have recently been made the apparatus was arranged as shown in fig. 1. The electrodes were symmetrical about the line joining the centres of the plate electrodes E_1 and F, and the figure represents a section of the apparatus through this line. The large electrode F was charged positively and attracted the electrons liberated from the electrode E_1 by a narrow beam

---

* E. W. B. Gill, Phil. Mag. xliii. p. 852, Nov. 1921.

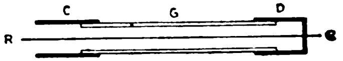
† J. S. Townsend and S. P. McCallum, Phil. Mag. [6] xlvii. p. 737 (1924).

‡ S. P. McCallum and C. M. Focken, Phil. Mag. [6] xlix. p. 1309 (1925).

of ultra-violet light. The light, emitted from the spark-gap S, entered the apparatus through a quartz window Q and passed through a long metal tube T attached to the lower plate F. The quartz window was sealed to a short length of tubing which dipped into a metal channel, where it was sealed in with lead. The aperture H in the plate F through which the light passed was 5 millimetres in diameter, so that nearly all the light entering the apparatus fell on a small area at the centre of the disk E_1. A ring electrode E_2 of internal diameter 3·5 centimetres and external diameter 6 centimetres was fixed in the same plane as the disk E_1. The diameter of the disk was 3·3 centimetres, which allowed a space one millimetre wide between the disk and the ring for insulation. A third electrode E_3, shaped as shown in the figure, extended from the plane of the electrodes E_1 and E_2 to the plane of the lower plate F. The electrode E_3 was insulated from E_2 by a narrow space one millimetre wide, and from the electrode F by a larger distance.

The electrodes E_1, E_2, and E_3 were mounted on a quartz rod q_1 of rectangular section, which was fixed at the ends to the upper plate A of the case. The electrode F was similarly mounted on two narrow quartz rods, q_2, q_3, fixed to the lower plate B of the case.

Fig. 2.



Connexion to the electrodes was made by the rods R_1, R_2, R_3, and R_4, which passed through long glass tubes G, as shown in fig. 2. The glass tubes were sealed at both ends to copper tubes C and D, and the rods R were soldered to disks which closed the ends of the tubes D. The tubes C were soldered to the case of the instrument in the positions C_1, C_2, C_3, and C_4, shown in fig. 1. A copper glass seal was also used for connecting the glass tubing which led from the apparatus to the pressure gauge and the charcoal tubes in which the gases were purified. All the electrodes and the metal case of the instrument were of brass which was silver-plated.

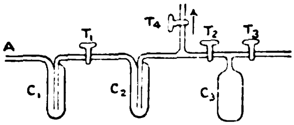
16. Thus the whole apparatus was made up entirely of glass, quartz, and metal parts, and it was possible to heat it up to a temperature of about 100° C. to expel gas from the

metal surfaces. The temperature was limited by the melting-point of the soft solder which it was necessary to use in connecting the tubes C to the case. After exhausting the apparatus and heating it for several hours there was found to be a very small leak in the case, but it was made absolutely air-tight by covering the soldered junctions on the outside with a hard wax cement.

Any remaining trace of impurity in the apparatus was removed by washing it out with some of the pure gas, and when this was done, the effect of impurities from the metal surfaces was so small that no change was observed in the electrical properties of the gas after keeping it in the apparatus for several days.

The gases used were helium and neon, from which nearly all impurities may be removed by charcoal cooled with liquid air. In order to make sure that the gases were free from hydrogen, they were introduced into a glass vessel with oxygen obtained by electrolysis of barium hydrate, and a discharge was passed through the mixture for about twenty hours. The vessel contained phosphorus pentoxide to absorb any water vapour which might be formed. The gas was then passed slowly over copper-foil heated in quartz tubes, to remove the oxygen, and from these tubes it was admitted into a tube containing charcoal cooled with liquid air. The gas was then pumped into flasks with mercury-sealed taps. Most of this work was done by Mr. McCallum, as he also required some of these gases for experiments which will be described in another paper.

Fig. 3.



The neon used in these experiments was given to us by M. Georges Claude. The only impurity in it was a small quantity of helium, probably less than one per cent. of the neon.

The apparatus shown in fig. 1 was connected to the tube A, fig. 3, leading through small charcoal tubes C_1 and C_2 to the large charcoal tube C_3 with mercury-sealed taps T_2 and T_3 on either side. The apparatus was exhausted through the tap T_4 which led to the mercury gauge and the pump. Gas from the containing flask was admitted to the tube C_3 to a pressure of about 300 millimetres, and the three charcoal tubes were cooled with liquid air for about twelve hours before the gas used in an experiment was admitted to the apparatus. The space between the taps T_1, T_2, and T_4 was used for taking small quantities of gas from the large tube C_3.

In order that no mercury vapour from the gauge should get into the apparatus while taking the pressure, the pressure in the gauge was reduced before opening the tap T_4. Thus the stream of gas always went in the direction of the arrow through the tap T_4.

17. The dimensions and positions of the electrodes were determined by the following considerations. The electrodes E_1, E_2, and E_3 were at zero potential throughout, and F at a positive potential V, so that when the beam of ultra-violet light from S falls on E_1, the electrodes E_2 and E_3 may acquire positive charges, by positive ions arriving from the gas or by the escape of negative electricity due to the photo-electric effect of radiation from the gas. The principal current flows from E_1 to F. The stream of electrons set free from the centre of E_1 diverges and falls on a large area of the electrode F. When the potential V is increased molecules of gas are ionized, and the positive ions received by E_1 are distributed over a much wider area than that from which the electrons were set free. The diameter of E_1 was determined so that in helium nearly all the positive ions should fall on this electrode for considerable ranges of the electric forces and gas pressures. An approximate estimate of the minimum diameter which would satisfy this condition was obtained from the results of the experiments on the divergence of streams of electrons in helium. The diameter 3·3 cm. may appear to be too small as the distance between the electrodes is 2·55 cm., but in these experiments the electrons start from the negative electrode with very small kinetic energy, and with the smaller forces they do not acquire the energy of agitation of the steady motion corresponding to the electric force until they have traversed a considerable part of the distance between the electrodes. In the first part of the path the lateral diffusion of the stream is therefore comparatively small, and in the neighbourhood of the electrode F, the electrons are not so widely distributed as they are in the experiments where they pass through a slit in the negative electrode with the energy of agitation of the steady motion corresponding to the electric force.

The divergence of the stream increases as the pressure is reduced and is greater in neon than in helium, so that in helium at the lower pressures some of the positive ions are received on the ring electrode E_2, and in neon they may extend to both electrodes E_2 and E_3.

The solid angles subtended by the electrodes E_1, E_2, and E_3 at the centre of the plate F are $2\pi\times{\cdot}17$, $2\pi\times{\cdot}19$, and $2\pi\times{\cdot}64$ respectively, so that if radiation were given out uniformly in all directions from the centre of the plate F, these numbers represent the proportion in which the energy would be received by the three electrodes. In the initial stages of the development of large currents, radiation from the gas due to collisions of electrons with molecules would come from points near the electrode F, and the number of electrons it would set free from the three electrodes would be approximately proportional to the above numbers. Thus about the same number would be set free from the disk E_1 and the ring electrode E_2, and about three times as many from the large electrode E_3.

18. Let n_1, n_2, and n_3 be the currents to the three electrodes, and N_1 the current comprising the electrons set free from the centre of the disk E_1 by the beam of ultra-violet light from the spark-gap S. The quantity N_1 increases with the electric force and it cannot be found accurately by these experiments. The ratio n_1/N_1 for several values of the potential V has been found by other experiments, but for the purpose of this investigation it is unnecessary to obtain the exact value of N_1.

If the increase of current (n_1-N_1) be due to ionization of the gas by collisions of electrons with molecules in the path of the original stream N_1, then (n_1-N_1) would be large compared with n_2 or n_3.

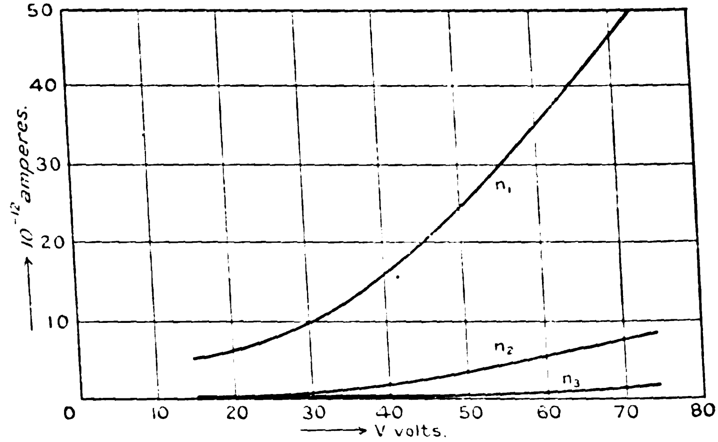
If the increase of current (n_1-N_1) be due to a photoelectric effect of radiation from the gas then (n_1-N_1) would be approximately equal to n_2, and n would be about three times as great as (n_1-N_1) or n_2.

The currents n_1, n_2, and n_3 to the electrodes were determined with the plate F at various potentials from 16 to 80 volts, for different gas pressures. The currents were measured by an induction balance, using a sensitive electrometer as an indicator. By this method the potential of the electrode does not vary more than one-tenth of a volt from the zero potential during the course of a measurement. In all cases the current n_3 was found to be small compared with n_1, and it is clear that in helium 99 per cent. of the increase of current (n_1-N_1) for the range of potentials used must be due to ionization of molecules of the gas by collisions with electrons.

In neon it is not possible to obtain an upper limit of the effect of radiation as accurately as in helium, but it may be seen that it does not exceed 5 per cent. of the effect of ionization by collision.

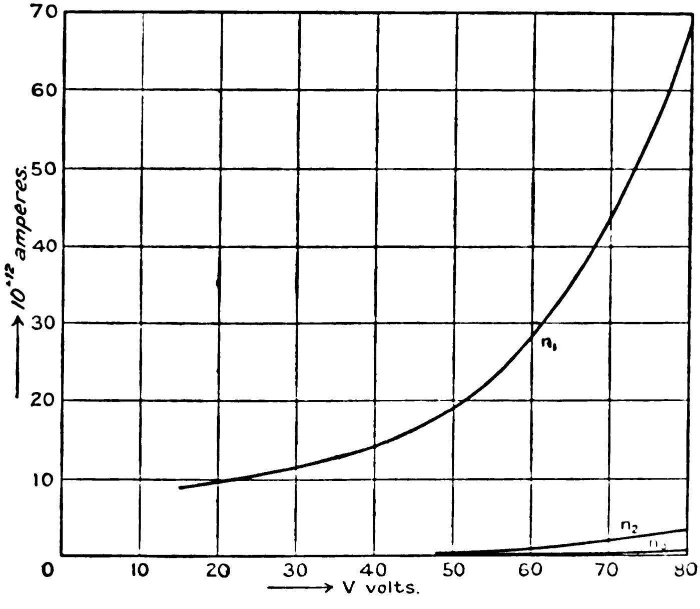
The experiments with helium were made at pressures of 2, 4, 8, and 16 millimetres. The increase of current with the potential V was greater at 4 millimetres pressure than at the other pressures. At 16 millimetres the increase of current was comparatively small. The currents obtained at the pressure 2 mm. are given by the curves fig. 4, and those at 8 mm. by the curves fig. 5. The ordinates of the curves n_1, n_2, and n_3 are the currents to the three electrodes, the abscissæ being the potentials of the electrode F in volts.

Fig. 4.—Helium. $p=2$ mm.



The principal difference between the results obtained at these two pressures is in the current n_2 to the ring electrode. At the lower pressure the stream of electrons from E_1 is so divergent that a larger proportion of positive ions are received on the electrode E_2. At 2 millimetres pressure the current n_1 is about twice the current N_1 at the potential $V=45$ volts, as found by other experiments, so that in the units in which the currents are given (n_1-N_1) is 10. Most of the small current n_3 is due to electrons set free from the electrode E_3 by scattered light from the original beam, since a current to this electrode is obtained when V is 16 volts. Like the main current n_1, the small current n_3 increases with the potential V. At the point $V=16$ the current n_2 is about ·12, and at V=45 about ·55. The current at the latter potential to be expected from the normal increase of the current ·12 is about ·5. Hence at the point V=45 volts the current to the electrode E_3, which may be attributed to radiation from molecules of the gas, cannot exceed ·1, and one-third of this amount represents the effect which radiation from molecules of the gas may have at the electrode E_1. Thus the photo-electric effect due to radiation from molecules of the gas cannot be as much as one per cent. of the effect of ionization by collision in increasing the current n_1.

Fig. 5.—Helium. $p=8$ mm.



At the higher pressures the effect of radiation from molecules of the gas is even less than at 2 millimetres.

The results of the experiments with helium at 4 millimetres pressure are given by the figures in Table I., as the currents cannot be compared very accurately by the curves. The potentials V are given in volts, and the unit of current is 10^{-12} ampere.

Experiments were also made with neon at the pressures 2, 4, 8, and 16 millimetres. In this gas the effect of change of pressure on the conductivity is not so great as in helium.

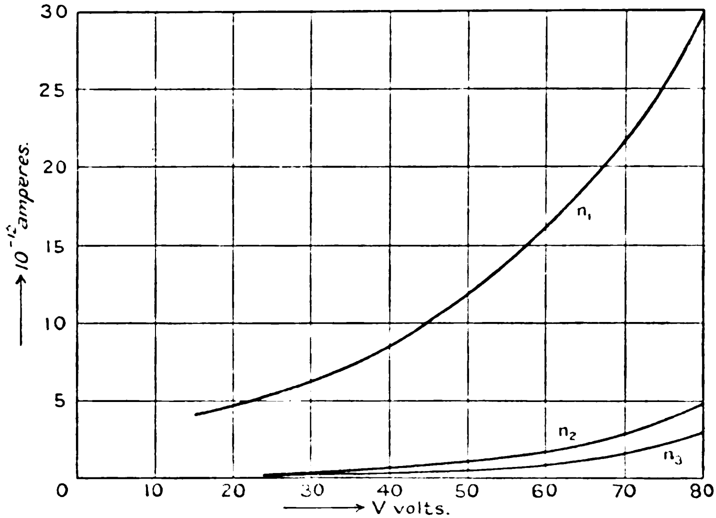
Also the effect of lateral divergence due to diffusion is greater than in helium, as is shown by the comparatively large current n_2 to the ring electrode E_2, which at the lower pressures was as great at 14 per cent. of the total current. The best conductivity was obtained with the gas at 16 millimetres pressure, and the currents n_1, n_2, and n_3 for this pressure are represented in terms of the potential V by the curves fig. 6.

Table I.

Helium, 4 mm. pressure.

V………	16	30	40	48	60	72
$\frac{X}{p}$ ……	1·57	2 94	3·92	4·71	5 9	7·1
n_1 ……	6·4	10·1	16·5	22·8	41·2	58·2
n_2 ……	—	·10	·94	1·9	4·8	7·23
n_3 ……	·08	·11	·21	·32	·62	·90

Fig. 6.—Neon, $p=16$ mm.'



In this gas, although an increase in current due to ionization by collision is more marked than in helium when the potential V is 20 volts, a potential larger than 45 volts is required to double the initial current N_1. At the potential 55 volts n_1 is about double N_1, so that at this point of the curve $(n_1 - N_1)$ is 7 units, and n_3 is ·7 unit.

As the current n_3 is an upper limit to the photo-electric effect on the electrode E_3 due to radiation from the gas, one-third of this current is an upper limit to the effect of radiation from the gas on the electrode E_1. So that this effect is less than 5 per cent. of the effect of ionization by collision in the increase of the current n_1. At the point $V=55$ volts the current n_2 is 1·4, and n_3 is ·7. The part of the current n_2 due to positive ions generated by the stream N_1 is approximately $\left(n_2 - \frac{n_3}{3}\right) = 1·2$, which indicates a very wide distribution of the positive ions. Consequently a part of the current n_3 must be attributed to positive ions, and the actual value of the photo-electric effect may be considerably below the upper limit given above.

The results of the experiments with neon at 8 millimetres pressure are given by the figures in Table II., the units of potential and current being the same as in Table I.

TABLE II.

Neon, 8 mm. pressure.

V........	24	48	60	72	80
$\frac{X}{p}$	1·18	2·36	2·94	3·53	3·92
n_1	5·3	11·0	15·6	20·9	25·3
n_2	·24	1·31	2·01	3·04	4·28
n_3	·12	·69	1·27	2·08	3·08

The following conclusions may therefore be drawn from these and other experiments on the conductivity between parallel plates. A definite increase in current due to ionization by collisions may be obtained in helium with potentials as low as 21 volts and in neon with potentials as low as 17 volts. These numbers are upper limits of the ionizing potentials. The increase of current which may be attributed to a photo-electric effect of radiation from molecules of the gas is small compared with the increase of current due to ionization by collision.

XL. *Notices respecting New Books.*

Summation of Series. By L. B. W. Jolly, M.A. (Chapman & Hall. 13*s.* 6*d.*)

THE author has made a very extensive collection of results from various mathematical sources, commencing with the simple progressions and the sums of powers and products of natural numbers. It is interesting to note in this connexion that the values of some oscillating series, *e. g.* $1-3+6-10+\ldots\ldots\infty$, are given; the summation is easily made by the method of differences. An extreme example of this character occurs on page 164, where Euler's value of the series $1!-2!+3!-4!+\ldots\ldots\infty$ is given as calculated from a continued fraction. Further series are related to the exponential and logarithmic functions and other power series, in some of which the numbers of Bernouilli and Euler appear. Nearly half the book is devoted to trigonometrical and hyperbolic summation, which should be of use in the solution of various technical problems. A passing reference is given to the Gamma, Elliptic, Bessel and other functions. Blank pages are left for the insertion of further results. The bibliography gives a list of the authorities consulted in the preparation of this valuable collection.

Four-figure Mathematical Tables. Kaye and Laby. (Longmans Green & Co. 1*s.*)

A useful and inexpensive set of logarithmic and other tables. In addition to the ordinary tables of logarithms to four and five places, the series includes tables of the natural trigonometric functions with their logarithms, reciprocals and squares, and a table for the conversion of degrees of angles to radian measure. Values of some of the simple functions of π and e are also given with the logarithms to five places of decimals.

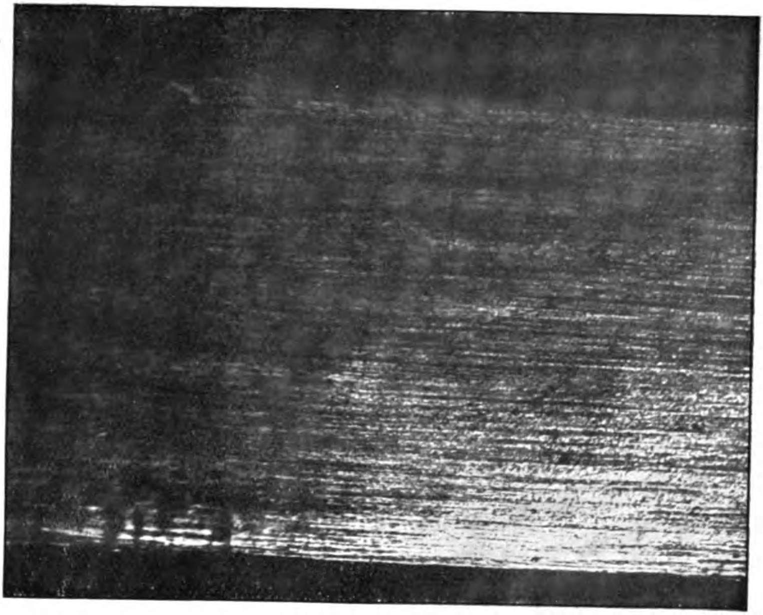
The Nervous Mechanism of Plants. By Sir Jagadis Chunder Bose. (Longmans, Green & Co. 1926. 16*s.* net.)

Sir J. C. Bose has done important pioneer work in scientific biology, and the present volume gives a further instalment of the researches which he is carrying on at the Bose Institute, Calcutta. The results of his investigations during the last twenty-five years tend to establish the theory that the physiological mechanism of the plant is identical with that of the animal. In the present work it is shown that not only has a nervous system been evolved by the plant, but that it has reached a very high degree of perfection, as marked by the reflex arc in which a sensory becomes transformed into a motor impulse. There is no doubt that the broader outlook which regards physiological mechanism as one unified class of problems whether they belong to plants or animals will lead to a great advance in physiological research and our knowledge of the irritability of all living tissue.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

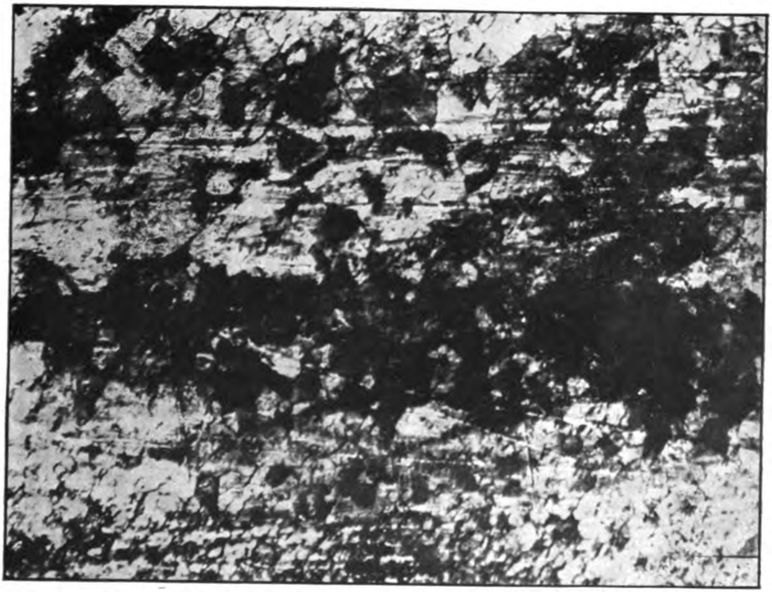
A. PHOSPHOR-BRONZE STRIP (unannealed).

[Shows marked variation of rigidity.]



B. PHOSPHOR-BRONZE STRIP (annealed).

[Shows only slight variation of rigidity.]



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

SEPTEMBER 1926.

XLI. *On the Condenser-Telephone.* *By* G. Green, *D.Sc., Lecturer in Physics in the Applied Physics Department of the University of Glasgow*[*].

IN 1863, in a letter from Prof. Sir William Thomson[†] to Professor Tait, there is a reference to the sounds produced by a condenser when charged and discharged. The possibility of constructing a telephone by employing the sheets of a condenser as the vibrating mechanism for transmitting sound was recognized very soon after. Condenser-telephones were made by Varley and by Dolbear about the year 1870, and later by Pollard and Garnier. In the years from 1870 to 1890 numerous attempts were made to produce condenser-telephones which might compete with the electromagnetic telephone. These condenser-telephones were intended for use as ear-phones, and the capacities of the instruments must have been exceedingly small in hand-instruments of this type. This in part explains why the sounds transmitted by them were feeble compared with the sounds transmitted by the ordinary electromagnetic telephones, as we shall see in the discussion to be given later. References are to be obtained to condenser-telephones of the same type at intervals up to the present time, one of the chief instruments described being that by Ort and Rieger in 1907.

---

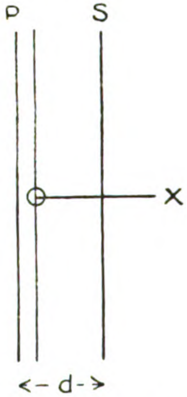
[*] Communicated by the Author.

[†] Lord Kelvin's Papers on Electrostatics and Magnetism, § 302.

From some preliminary experiments* which have been made with condensers of a larger type it appeared that the condenser could be made an instrument for transmitting sound of great efficiency as well as one of exceedingly high quality, and the author was induced to carry the investigation further. In the present paper it is proposed to give a preliminary discussion of the mathematical theory of the condenser-telephone when used either as a receiver or as a transmitter. The condenser-telephone transmitter has been in use now for a considerable time, but I am not aware of any complete mathematical discussion of the transmitter applicable to the type of condensers employed in the experiments.

We take first the case of the condenser-telephone receiver. The essential feature required in the condenser is that its plates should be so mounted as to be free to vibrate, and this condition can be fulfilled whether the bounding edges of the plates be free or fixed. There is thus a large number of special cases to be considered depending upon the nature of the elastic restoring force acting upon each plate when disturbed from its equilibrium position. We wish, however, at first simply to investigate the main qualities and possibilities of the condenser as an instrument for reproducing sound and speech, and to indicate the theory used as a guide throughout the experimental investigations. For our present purpose it is sufficient to take the case of a condenser consisting of two metal sheets P and S, having a uniform sheet

Fig. 1.



---

* During the early part of the experimental work connected with this investigation I had valuable assistance from Alexander J. Younger, M.A., B.Sc., of this Department.

of dielectric material completely occupying the interspace between them. One of the metal sheets, S, may be regarded as fixed in position in a vertical plane, with the dielectric sheet just in contact with both metal plates, but not exerting any force upon either of them, when the condenser is uncharged. In any actual condenser separate sheets of material of the type considered would not have perfect contact one with the other, and part of the interspace between the plates would always be occupied by air, even when the sheets are laid horizontally and put under pressure. Thus the force acting upon the plate P when disturbed from its equilibrium position would not be wholly due to the elastic resistance of the dielectric material interposed between the metallic plates but in part to the resistance to compression of the layer of air included with the dielectric material. The dielectric may of course be air alone. Nevertheless, for the sake of simplicity in what follows we shall treat the material in the interspace as acting when under pressure like an elastic medium having a Young's Modulus Y.

When the condenser is charged, the metal plates attract each other and the dielectric is compressed by an amount depending upon the charge upon each plate. If d be the original distance apart of the plates, and a the amount the plate P moves towards plate S due to a fixed charge Q_0, we have

$$YA\frac{a}{d}=\frac{2\pi Q_0^2}{Ak}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

A being the area of each plate, and k being the specific inductive capacity of the dielectric. Let now the position of plate P when Q_0 is the charge upon each plate be taken as origin, and let x denote the distance of plate P from the origin at any later time, x being positive for a motion of plate P towards plate S. Assuming now that the total charge on each plate at any instant Q is represented by $Q=Q_0+q$, where q is a small quantity of the type $b\sin(\omega t+e)$, we have to determine the corresponding motion of the plate P. This motion will be resolvable into a series of simple harmonic motions about a mean position, each of which motions is communicated to the air on the open side of the plate P. It is easy to show that the force applied by the air in contact with the plate is equivalent to a resisting force which can be represented by $\kappa\dot{x}$, where κ is a constant which we shall determine later from hydrodynamical considerations. The equation of motion of plate P can now be written in the form

$$m\ddot{x}+\kappa\dot{x}+\mathrm{YA}\frac{a+x}{d}-\frac{2\pi\mathrm{Q}^2}{\mathrm{A}k}=0, \quad . \quad . \quad . \quad (2)$$

where m is the total mass of the plate. As we employ electromagnetic units below, we now replace Q by $\mathrm{Q}v$, where v is the velocity of light. In virtue of equation (1) the above may be written in the form

$$m\ddot{x}+\kappa\dot{x}+\mathrm{YA}\frac{x}{d}-\frac{4\pi\mathrm{Q}_0v^2}{\mathrm{A}k}q-\frac{2\pi v^2}{\mathrm{A}k}q^2=0, \quad . \quad . \quad (3)$$

q being a quantity which remains to be determined by consideration of the electrical conditions obtaining in the condenser circuit.

A typical condenser-telephone circuit would consist of a condenser, whose capacity when the plate P is at the origin we may represent by C_0, a transformer secondary coil of inductance L in series with the condenser, and a battery of e.m.f. E, the total resistance of the circuit being represented by R. If we assume that a small variable e.m.f. $e\sin\omega t$ is applied to this circuit by means of the transformer, the equation determining the total charge Q at any instant on each condenser plate is given by

$$\mathrm{L}\frac{d^2\mathrm{Q}}{dt^2}+\mathrm{R}\frac{d\mathrm{Q}}{dt}+\frac{\mathrm{Q}}{\mathrm{C}}=\mathrm{E}+e\sin\omega t \quad . \quad . \quad . \quad (4)$$

If we take $\mathrm{Q}_0=\mathrm{C}_0\mathrm{E}$, the charge on each plate produced by the battery e.m.f. E acting alone, we have $\mathrm{Q}=\mathrm{Q}_0+q$ and q is determined by

$$\mathrm{L}\frac{d^2q}{dt^2}+\mathrm{R}\frac{dq}{dt}+\frac{\mathrm{Q}_0+q}{\mathrm{C}}-\frac{\mathrm{Q}_0}{\mathrm{C}_0}=e\sin\omega t. \quad . \quad . \quad (5)$$

At any instant t, the moving plate P is in the position x, and the capacity of the condenser is then given by

$$\mathrm{C}=\frac{\mathrm{A}k}{4\pi(d-a-x)v^2}=\mathrm{C}_0\left(1+\frac{x}{d-a}\right),$$

so that the equation to determine q is finally obtained in the form

$$\mathrm{L}\frac{d^2q}{dt^2}+\mathrm{R}\frac{dq}{dt}+\frac{q}{\mathrm{C}_0}=e\sin\omega t+\frac{\mathrm{E}}{d-a}x \quad . \quad . \quad . \quad (6)$$

We may assume that x can be represented by

$$x=\mathrm{X}\sin(\omega t+\epsilon),$$

and the solution of this equation can then be written down as

$$q = \alpha\left\{e\sin\omega t + \frac{\mathrm{EX}}{d-a}\sin(\omega t+\epsilon)\right\}$$

$$-\beta\left\{e\cos\omega t + \frac{\mathrm{EX}}{d-a}\cos(\omega t+\epsilon)\right\},$$

where

$$\alpha = \frac{\mathrm{C}_0(1-\mathrm{LC}_0\omega^2)}{\{(1-\mathrm{LC}_0\omega^2)^2+\mathrm{R}^2\mathrm{C}_0{}^2\omega^2\}} = \frac{\mathrm{C}_0\cos\theta}{\sqrt{\{(1-\mathrm{LC}_0\omega^2)^2+\mathrm{R}^2\mathrm{C}_0{}^2\omega^2\}}},$$

$$\beta = \frac{\mathrm{RC}_0{}^2\omega}{\{(1-\mathrm{LC}_0\omega^2)^2+\mathrm{R}^2\mathrm{C}_0{}^2\omega^2\}} = \frac{\mathrm{C}_0\sin\theta}{\sqrt{\{(1-\mathrm{LC}_0\omega^2)^2+\mathrm{R}^2\mathrm{C}_0{}^2\omega^2\}}},$$

and

$$\tan\theta = \frac{\mathrm{RC}_0\omega}{(1-\mathrm{LC}_0\omega^2)}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The value of q is accordingly obtained as

$$q = \frac{e\mathrm{C}_0\sin(\omega t-\theta)}{\sqrt{\{(1-\mathrm{LC}_0\omega^2)^2+\mathrm{R}^2\mathrm{C}_0{}^2\omega^2\}}} + \frac{\alpha\mathrm{E}}{(d-a)}x - \frac{\beta\mathrm{E}}{\omega(d-a)}\dot{x}, \quad (8)$$

and we have to insert this value of q in equation (3) above, and determine the corresponding value of x.

As we have assumed that q is a small quantity of the first order of smallness compared with Q_0, we at present omit the term $\frac{2\pi v^2}{\mathrm{A}k}q^2$ in equation (3). When we insert the value of q given above, and replace $\frac{4\pi\mathrm{Q}_0v^2}{\mathrm{A}k}$ by $\frac{\mathrm{E}}{d-a}$, this equation becomes

$$\ddot{x} + \mathrm{K}\dot{x} + n^2x = \mathrm{B}\sin(\omega t-\theta),$$

where

$$\mathrm{K} = \left[\frac{\kappa}{m} + \frac{\mathrm{E}^2\mathrm{C}_0\sin\theta}{\omega m(d-a)^2\sqrt{\{(1-\mathrm{LC}_0\omega^2)^2+\mathrm{R}^2\mathrm{C}_0{}^2\omega^2\}}}\right],$$

$$n^2 = \left[\frac{\mathrm{YA}}{md} - \frac{\mathrm{E}^2\mathrm{C}_0\cos\theta}{m(d-a)^2\sqrt{\{(1-\mathrm{LC}_0\omega^2)^2+\mathrm{R}^2\mathrm{C}_0{}^2\omega^2\}}}\right],$$

$$\mathrm{B} = \frac{e\mathrm{EC}_0}{m(d-a)\sqrt{\{(1-\mathrm{LC}_0\omega^2)^2+\mathrm{R}^2\mathrm{C}_0{}^2\omega^2\}}}. \quad . \quad . \quad . \quad (9)$$

The solution of equation (9) takes the well-known form

$$x = \frac{\mathrm{B}}{\sqrt{\{(n^2-\omega^2)^2+\mathrm{K}^2\omega^2\}}}\sin(\omega t-\theta-\phi)\,; \quad \tan\phi = \frac{\mathrm{K}\omega}{(n^2-\omega^2)} \quad . \quad . \quad . \quad (10)$$

for the case where n^2 is a positive quantity. We are concerned chiefly with the amplitude of the motion of the plate P, which is accordingly represented by

$$\text{amp.} = \frac{eEC_0}{m(d-a)\sqrt{\{(1-LC_0\omega^2)^2+R^2C_0^2\omega^2\}\{(n^2-\omega^2)^2+K^2\omega^2\}}}. \quad . \;. \;. \quad (11)$$

The above solution applies to the most important case in practice of the use of a condenser as a receiver, namely, that in which a considerable steady voltage is applied to the condenser plates in addition to the varying voltages applied through the action of the transformer coil in transmitting electrical vibrations from the primary to the condenser circuit. The corresponding results for the case where $E=0$ and where the term $\frac{2\pi q^2}{Ak}$ is retained, can readily be obtained from the equations given above.

Before entering into the discussion of the above solution it is convenient to derive the corresponding solution for the case of a condenser used as a transmitter. In this case we assume that an external force represented by $M\sin\omega t$ is applied to the plate P of the condenser, and the problem is to determine the amplitude of the electrical vibrations thereby produced in the condenser circuit, and transmitted to a secondary circuit by the transformer. Instead of the equation of motion of plate P given by (3) above, we have now

$$m\ddot{x}+\kappa\dot{x}+YA\frac{x}{d}-\frac{4\pi Q_0}{Ak}v^2q-\frac{2\pi}{Ak}v^2q^2=M\sin\omega t. \quad (12)$$

Instead of the circuit equation given by (6) above, we have now

$$L\frac{d^2q}{dt^2}+R\frac{dq}{dt}+\frac{q}{C_0}=\frac{E}{(d-a)}x, \quad . \;. \;. \;. \quad (13)$$

so that the value of q the variable part of the condenser charge is again given by equation (8) with e equal to zero. The equation to determine x corresponding to equation (9) above is

$$\ddot{x}+K\dot{x}+n^2x=\frac{M}{m}\sin\omega t, \quad . \;. \;. \quad (14)$$

where K and n^2 have the values indicated in equation (9).

The solution of (14) gives x the displacement of plate P at time t in the form

$$x=\frac{M}{m\sqrt{\{(n^2-\omega^2)^2+K^2\omega^2\}}}\sin(\omega t-\phi)\;;\quad \tan\phi=\frac{K\omega}{(n^2-\omega^2)}, \quad . \;. \;. \quad (15)$$

and the variable charge on the condenser, q, arising from the application of the external force $M \sin \omega t$ is represented by

$$q = \frac{MEC_0 \sin (\omega t - \phi - \theta)}{m(d-a) \sqrt{\{(1-LC_0\omega^2)^2 + R^2C_0^2\omega^2\}\{(n^2-\omega^2)^2 + K^2\omega^2\}}} . \quad . \quad . \quad . \quad (16)$$

From this the value of the current in the condenser circuit can be readily derived, if required. The corresponding solution for the case where $E=0$ can be worked out from the above equations, but it is not of so much value in practice.

The main results with which we are concerned are contained in equations (9), (11), and (16). These equations show that the best conditions of working of a condenser-telephone either as a receiver or as a transmitter depend upon the values chosen for the frequency of mechanical vibration represented by $\frac{n}{2\pi}$, and for the frequency of electrical vibration of the condenser circuit represented by the value of $\frac{\omega}{2\pi}$ which makes $\{(1-LC_0\omega^2)^2 + R^2C_0^2\omega^2\}$ a minimum. In what follows we shall confine our attention to the case of the receiver as indicated by equations (9) and (11), as it is easy to derive the corresponding results for the transmitter from equations (15) and (16).

We may regard $\frac{\omega_0}{2\pi}$ as the natural frequency of the condenser circuit, where $LC_0\omega_0^2 = 1$. If the vibrations imposed upon the condenser circuit are of frequency $\frac{\omega_0}{2\pi}$, we have electrical resonance and $\cos \theta$ is then zero. The frequency of vibration of the condenser plate is then given by

$$\frac{n}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{YA}{md}},$$

in which Y is a constant depending upon the elastic resistance of the dielectric material to compression and upon the resistance to compression of the air imprisoned between the plates of the condenser. As the values of Y have not yet been obtained experimentally, we may estimate that a lower limit for its value would be obtained by taking the dielectric to be air completely imprisoned between the plates.

This gives $Y=\gamma\pi$, where π is atmospheric pressure, or $Y=1{\cdot}42\times10^6$ dynes per square centimetre. In a condenser composed of tinfoil sheets of mass ·005 gram per sq. cm. set so as to be ·003 cm. apart, n^2 is of the order 9×10^{10}. When the condition for electrical resonance is not fulfilled, the term in $\cos\theta$ must be included in evaluating n^2. As the frequency of the imposed vibrations rises above resonance frequency, the value of n^2 increases, and as the frequency of the imposed vibrations falls below resonance frequency the value of n^2 decreases. In this way the mechanical frequency of the condenser plate tends to accommodate itself to suit a wide range of frequency in the vibrations imposed upon the condenser, so that it is impossible for any sharp resonance conditions to exist at any given frequency of the applied vibrations. The electrical frequency of the condenser circuit can be made to agree with the frequency of the most powerful tones of the human voice without any of the usual effects of resonance being evident *.

Consider now the resistance coefficient K. Of the total resistance to the motion of the condenser plate at any instant $mK\dot{x}$, the part $\kappa\dot{x}$ represents the force communicated by the moving plate to the air in contact with it. The motion communicated to the air in the problem which we have been considering consists of a progressive train of waves which may be represented by a velocity-potential $\phi=a\cos\{\omega(x-Vt)\}$, where V indicates the velocity of sound in air. From this we can easily obtain the velocity of an air particle as $-\omega a\sin\{\omega(x-Vt)\}$, and the pressure increase per unit area at plane x by $-\dot{\omega}\rho_0Va\sin\{\omega(x-Vt)\}$, where ρ_0 is the density of undisturbed air. Thus the force acting on any plane of area A at x is $A\rho_0V\dot{x}$ and the value of the coefficient $\frac{\kappa}{m}$ is therefore $\frac{A\rho_0V}{m}$, which is equivalent to $\frac{4{\cdot}2A}{m}$. This can be increased by diminishing the mass per unit area of the plates. The remaining part of the coefficient K represented by the term containing $\sin\theta$ has clearly a maximum value at the frequency $\frac{\omega_0}{2\pi}=\frac{1}{2\pi\sqrt{LC_0}}$ which is the frequency at which there is electrical resonance. The value of the term containing $\sin\theta$ in the coefficient K rapidly falls off as the frequency passes away from the value

---

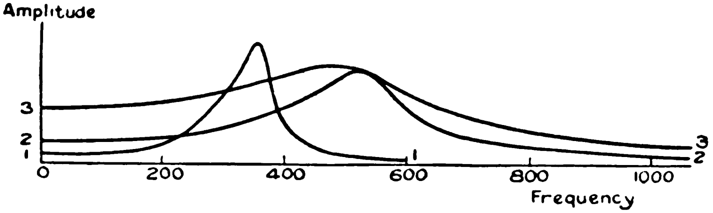
* See "Analysis of Energy Distribution in Speech," by Crandall & McKenzie, Physical Review, xix., 1922.

$\frac{\omega_0}{2\pi}$ corresponding to the condition of electrical resonance. At very high frequencies the term in $\sin\theta$ is zero, and practically all damping of the motion of the plate is then due to the communication of sound vibrations to the air. At frequencies below the resonance frequency $\frac{\omega_0}{2\pi}$, the term in $\sin\theta$ diminishes as ω diminishes, rapidly at first and then gradually, reaching the constant value $\frac{E^2RC_0^2}{m(d-a)^2}$ when $\omega=0$. The damping coefficient accordingly varies with the frequency of the imposed vibrations, and is of importance over the whole range of frequency with which we are chiefly concerned in reproducing the human voice. It is to be noted, however, that the variation of the coefficient of resistance is favourable to the formation of a curve of amplitude against frequency which is exceedingly uniform over the range of frequency referred to above as the resistance falls off as the frequency of the applied vibrations passes away from the resonance value on either side.

Consider now the manner in which the amplitude term B of equation (9) varies with the capacity of the condenser, for all values of ω, subject to the condition that the frequency of the circuit $\frac{\omega_0}{2\pi}=\frac{1}{2\pi\sqrt{LC_0}}$ has a certain value assigned to it. When ω^2 is exceedingly large, B is proportional to C_0. When $\omega^2=\frac{1}{LC_0}$, which corresponds with the condition of resonance, B is proportional to $\frac{1}{R\omega_0}$. When ω^2 is less than ω_0^2 and is tending toward the value zero, B tends to become proportional to C_0. Thus when the frequency of the imposed vibrations is in the neighbourhood of the frequency of the condenser circuit, the amplitude of the motion of the condenser plate is independent of the value of the capacity of the condenser C_0. When, however, the imposed vibrations are of low frequency, the amplitude of the motion of the condenser plate depends directly on the value of the capacity of the condenser. This then is the explanation why the early condenser-telephones could only respond feebly to the human voice, for the capacities of the condensers used were exceedingly small and the lower and more important frequencies in the sound issuing from the condenser plates correspondingly weak. In the case of the receiver and also of the transmitter, the value of the capacity of the condenser C_0 must be properly chosen to keep the correct relation between the low and high frequency sounds of the transmitted speech. When the value of the frequency of the condenser circuit, $\frac{\omega_0}{2\pi}=\frac{1}{2\pi\sqrt{LC_0}}$, is already fixed for a given type of condenser, the determination of the most suitable value to use for the capacity of the condenser is a matter for experiment. With C_0 very small low frequency sounds are feebly reproduced, and with C_0 very large the low frequency sounds may be too strongly reproduced, as compared with sounds of high frequency.

If a curve be drawn to show the relation between amplitude and frequency as indicated by equation (11), the curve would in general have two maxima corresponding approximately with the value of ω given by $\omega^2=\frac{1}{LC}$ and $\omega^2=n^2$ respectively. These two values or frequencies giving a maximum value to the amplitude can be made to coincide so as to give a single maximum of increased value. The two values of ω^2 referred to should be chosen if possible within the range of frequency which is of greatest importance in relation to the frequencies contained in ordinary speech, so as to make the amplitude curve as nearly as possible a uniform straight line over the important range of frequency. Examples of the curves of amplitude and frequency given by equation (11) are shown in fig. 2 for the frequency range 0 to 1000. These curves show only one maximum corresponding to $\omega^2=\frac{1}{LC_0}$, the maximum corresponding to $\omega^2=n^2$ being much beyond frequency 1000 for condensers with air as dielectric to which the curves

Fig. 2.



refer. The curve marked 1 1 corresponds to the conditions

$$\frac{\omega_0}{2\pi}=356, \quad \frac{m}{A}=\cdot005 \text{ grm.}, \quad C_0=\cdot2 \text{ mf.},$$

$$E=150 \text{ volts}, \quad R=200 \text{ ohms},$$

and the maximum ordinate of the curve represents a displacement of $\frac{7eE\,.\,10^{-26}}{m(d-a)}$ cms. The curves marked 2 2 and 3 3 are for condensers made of the same material, and having the same voltage applied to the plates, but the frequency of the condenser circuit is now 534 instead of 356. These curves show the effect of increase of capacity on the form of the amplitude curve, at a given frequency of the condenser circuit. The curve 2 2 corresponds to a capacity of ·4 microfarad and the curve 3 3 to a capacity of 1 microfarad. When the capacity is very small the amplitude curve has a fairly sharp maximum at resonance frequency. When C_0 is increased up to the value determined by $C_0=\frac{1}{R\omega_0}$ the amplitude curve becomes practically a uniform straight line parallel to the frequency axis for the range of frequency from zero to beyond the value $\frac{\omega_0}{2\pi}$, which can of course be chosen to include any desired range of freqnency. Increase in amplitude can be obtained by increasing the value of $\frac{m}{A}$, thus bringing down the frequency corresponding to $\omega^2=n^2$ nearer to the frequencies of ordinary speech.

The average amount of energy communicated to the air at any given frequency per unit of time, by a vibrating plate of area A, can be found from the expression $\frac{1}{2}\rho_0 V\omega^2 A \times (\text{amplitude})^2$. The sound emitted by a condenser accordingly depends directly on the area of the plate, and the advantage to be obtained by using condensers of large area and therefore large capacity becomes still more apparent than before. The theory which we have been discussing obviously applies with certain modifications to the case of a condenser consisting of a pile of alternately positive and negative plates. In this case the uppermost plate may be regarded as having a displacement approximately n times the displacement of a single plate relative to its nearest neighbour, where n is the total number of plates assumed large. The above expression shows that the energy communicated to the air by a pile of plates n in number would be n^2 times the amount of energy communicated by a single plate of the same area: and much more energy would be delivered to the air by a condenser of given capacity if its plates were arranged to form a pile than when the condenser consists of only two parallel plates.

The above preliminary discussion of the properties of the condenser-telephone seems to indicate that the instrument has, when properly designed, the most important quality required in a telephone, namely, that of reproducing the vibrations delivered to it uniformly and equally over a very great range of frequency. On the other hand, condenser-telephones of low capacity show decided resonance effects and may be used in bridge-measurements or in heterodyne reception of continuous waves. The results contained in equations (11) and (16) have been verified generally for a considerable range of values of capacity and of voltage, but the experimental verification is still incomplete. The high quality of the reproduction of speech and music by the condenser-telephone has also been amply demonstrated by the experiments which are in progress, and of which I hope to give an account later. Condenser-telephones have also been tested for nearly two years in their use as Loud-Speakers for wireless reception with very satisfactory results. The author hopes to continue the mathematical and experimental investigation of the condenser-telephone, and of questions relating to the condenser circuit, in a later paper.

I wish to take this opportunity of acknowledging my indebtedness to Messrs. Brittains Ltd., Cheddleton Paper Mills, near Leek, Staffordshire, who have very kindly provided me with material for the experimental investigation.

XLII. *Note on the High Frequency Oscillatory Discharge in Rarefied Gas.* *By* R. C. RICHARDS, *M.Sc.*[*]

[Plate VIII.]

THE familiar experiments which can be carried out by passing a high-tension discharge through rarefied gases are too well known to need any description, and it occurred to the writer to try the effect of a high-tension discharge, of an alternating character, of high frequency.

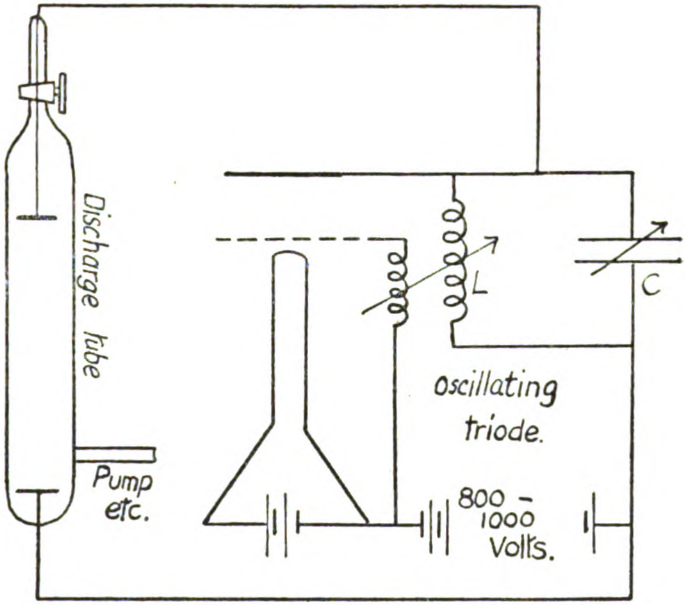
---

[*] Communicated by Prof. Alfred W. Porter, D.Sc., F.R.S.

The thermionic valve provided a ready source of high frequency oscillatory potential, which can be applied to the discharge-tube in the usual way. The diagram indicates the general method of connexion.

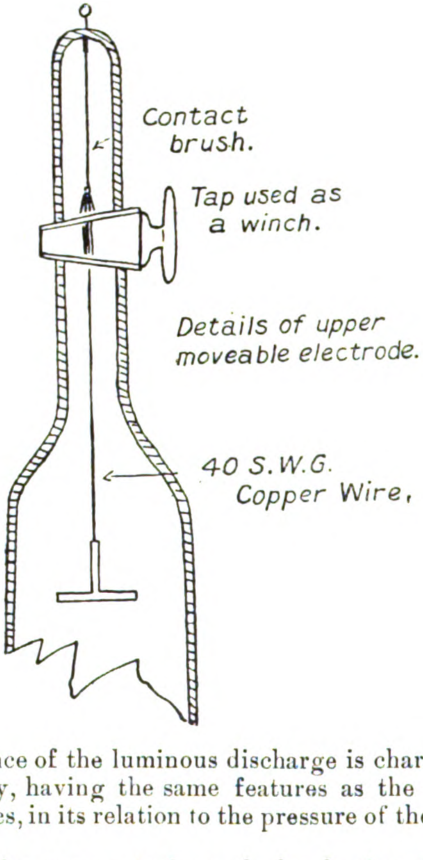
The power valve is provided with an inductance and capacity (L C) in the plate circuit, in series with a steady source of high potential of about 1000 volts, produced by a battery of small accumulators. The grid circuit consists of a reaction coil which can be so coupled to the inductance in the plate circuit as to set up powerful undamped oscillations in the plate circuit (L C), their frequency being given approximately by the formula $1/2\pi\sqrt{LC}$. The oscillating circuit is connected to the electrodes of the discharge-tube, and when this latter is exhausted to a sufficient degree, luminous discharge takes place.

Fig. 1



A special form of discharge-tube was used, with one fixed and one movable electrode. Thus the distance between the electrodes could be varied. The tube was used in a vertical position, the bottom electrode being fixed. At the top end of the tube an ordinary tap was sealed, the tap barrel having a groove filed in it carrying a thin copper wire from which was suspended the moving electrode. Thus the tap acted as a winch, winding up the wire and drawing up the electrode, or *vice versa*, a device due originally to Aston. Contact was made through the top of the tube remote from the discharge-tube, by means of a brush, touching the wire coiled on the tap barrel (fig. 2).

Fig. 2.



The appearance of the luminous discharge is characterized by its symmetry, having the same features as the ordinary direct discharges, in its relation to the pressure of the residual gas.

Both electrodes appear to be cathodes, having the usual negative glow and dark spaces, the positive column occupying the central region of the tube, if the electrodes are far enough apart. If they are relatively close together, the appearance of the discharge is that given by photograph I. (Pl. VIII). For relatively high pressures, separating the electrodes will cause the appearance of the continuous positive column.

The most interesting effects are obtained by having the pressure so adjusted as to give a striated positive column. Photograph II. shows the appearance of the tube when the electrodes are so far apart that the striated column is just appearing. It is seen that the striation is "double," consisting as it were of two striations placed back to back.

Hydrogen was the gas used in the tube, and the colour of this double striation was striking, having a pink edge to the usual blue colour of the hydrogen striation. Further separation of the electrodes produces more of these double striations, which seem to grow from the central pair as the electrodes are separated (photograph III.).

Photograph IV. shows the tube with the electrodes widely separated, and a whole series of double striations in the central column, the discharge about the electrodes being still characteristic of a cathode.

If the hand is placed near one end of the tube, the effect is altered considerably, indicating what a large effect the charges on the walls of the tube have on these discharge phenomena.

Photograph V. shows the appearance of the tube, with the hand placed near one end. It appears to cause a slight rectifying effect, for the luminosity round the electrode near the hand is very much diminished, and the striations have completely lost their double appearance.

Speculation on the nature of the double striation is rendered difficult, in the absence of any really decisive information as to the nature of the more frequently observed single striations. There is no doubt that they are of the same nature as these latter, and we may infer that one set belongs to the discharge when passing in one direction, and the other set is generated by the corresponding inverse discharge, the sharp convex surfaces being turned towards the corresponding cathode. The distance between the two members of the double striations can probably be regarded as the distance travelled by the positive ions in the tube during a half-period of the discharge, the frequency of which was of the order of 10^5.

The experiment described here is of a purely qualitative nature, but it opens up anew the question of the nature of the striated discharge, and further experiments on this point are now in progress.

Carey Foster Laboratory,
University College, London.

XLIII. *On the Theory of the Absorption of X-Rays.* By Dr. R. A. Houstoun, *Lecturer on Physical Optics in the University of Glasgow* *.

Introduction.

IT is possible, on the basis of the usual theory of dispersion, to calculate the number of electrons per molecule concerned in the production of an absorption band, such as the absorption bands in the spectra of the aniline colouring matters. I made this calculation in 1909 †, and found that these absorption bands were produced by one electron in each molecule and that the theory seemed to apply well in this case. When the formula was applied to inorganic salts such as cobalt chloride, the result suggested that in this case the vibrating systems were ions, though potassium permanganate was difficult to place. In 1919 ‡ I applied the same theory to the characteristic absorption of X-rays in nine elements, and found that there was one electron per atom concerned in the K absorption, and more—the results varied from two to four—concerned in the production of the L absorption. A. H. Compton § has since made calculations on the same lines. There is considerable doubt in the minds of many workers as to whether the ordinary theory, or, as it is sometimes called, the classical theory, can be applied to the absorption of X-rays, and as we have now additional data available, and I have arrived at a clearer understanding of the points involved, I desire to return to the subject here.

Proof of Formula.—Let a plane wave be passing through an absorbing medium. Let $Id\nu$ be the energy contained within the range of frequency (reciprocal of the period) $d\nu$, which passes through one square centimetre per second, and let

$$e^{-\mu z}$$

represent the rate of diminution of the intensity of the wave. μ is termed the "absorption coefficient."

The energy received on a parallel plate distant dz from the first one is

$$Id\nu e^{-\mu dz},$$

---

* Communicated by the Author.

† "On the Mechanism of the Absorption-Spectra of Solutions," Proc. Roy. Soc. A, lxxxii. p. 606 (1909).

‡ "The Absorption of X-Rays," Proc. Roy. Soc. Edin. xl. p. 34 (1919).

§ "Secondary Radiations produced by X-Rays," Bulletin of the National Research Council, 1922.

and the energy absorbed in the layer of 1 sq. cm. surface and thickness dz is

$$\mathrm{I}\,d\nu(1-e^{-\mu dz})=\mathrm{I}\,d\nu\,\mu\,dz.$$

Let N be the number of molecules per cubic centimetre. Then the number of molecules in the layer is Ndz and the amount of energy absorbed per molecule is

$$\frac{\mu\,\mathrm{I}\,d\nu}{\mathrm{N}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

§ Let us suppose that in the medium there are a number of electrons which execute vibrations about their mean positions under the influence of the wave. Then the motion of a typical electron may be represented by

$$m\frac{d^2x}{dt^2}+h\frac{dx}{dt}+fx=-e\mathrm{X}, \quad . \quad . \quad . \quad . \quad (2)$$

where m is the mass of the electron and X the electric intensity in the wave. The second and third terms represent the frictional resistance and the "quasi-elastic" force. Now the absorption of energy by the electron can be treated in two different ways. We may assume that the free vibration has died down, and that each of the Fourier components into which X can be resolved produces its own forced vibration. Consequently the electron never gains energy; it is being taken away from it as fast as it receives it. This is the usual method of the theory of dispersion, and it leaves the nature of the friction term a mystery.

On the other hand, we may suppose that there is no friction term, that initially the displacement and velocity of the electron are each zero, and that its kinetic energy gradually increases under the influence of the light-wave. Then there is a collision or atomic change that reduces its energy to zero, and the process starts over again. In this way the energy is removed from the electron discontinuously, not continuously. Strange to say, when the intensity I of the wave is given, the expression for the energy absorbed comes out the same on both assumptions.

§ It is not necessary to perform the calculation in the second case, for a similar calculation has already been performed by Planck, and our result can be obtained from his. Planck shows* that the energy absorbed by an oscillator per second is

---

* 'Vorlesungen über die Theorie der Wärmestrahlung,' §§ 148–9.

$$\frac{\mathfrak{J}}{4L},$$

where L corresponds to m/e^2 and $\mathfrak{J}$ is defined by

$$\overline{X^2}=\int_0^\infty \mathfrak{J}\,d\nu,$$

(*cf.* eqn. 2). The whole energy received per unit area is

$$\int_0^\infty I\,d\nu=\frac{c\overline{X^2}}{4\pi},$$

where c is the velocity of light. Consequently

$$I=\frac{c}{4\pi}\mathfrak{J},$$

and the energy absorbed per electron per second is

$$\frac{\mathfrak{J}}{4L}=\frac{\pi e^2 I}{mc}. \qquad \ldots\ldots\ldots \quad (3)$$

Let us suppose that there are p electrons per atom concerned in the absorption. Then from (3) and (1)

$$p=\frac{mc}{\pi e^2 N}\mu d\nu \quad \text{or} \quad p=\frac{mc}{\pi e^2 N}\int \mu d\nu, \qquad \ldots \quad (4)$$

if we integrate over the whole absorption band. We have tacitly assumed that e is measured in electrostatic units.

§ If we retain the friction term in (2) and assume forced vibrations, and $X=A\cos 2\pi\nu t$, we find

$$x=\frac{-Ae\cos\left(2\pi\nu t-\tan^{-1}2\pi\nu h/(f-4\pi^2\nu^2 m)\right)}{\left((f-4\pi^2\nu^2 m)^2+4\pi^2\nu^2h^2\right)^{\frac{1}{2}}}.$$

The rate at which work is being done on the electron is

$$-Xe\frac{dx}{dt}.$$

If we substitute in this expression for X and dx/dt, and take the average value, we obtain

$$\frac{A^2 2\pi^2\nu^2e^2h}{(f-4\pi^2\nu^2m)^2+4\pi^2\nu^2h^2}$$

Let us assume now that ν varies and graph the above expression as a function of ν. It will be found that the curve falls away rapidly on both sides of a maximum, the position of which we shall denote by ν_m, and that the only term of importance is the first one in the denominator. We may therefore substitute ν_m for ν in the other term in the denominator and for one of the ν's in the numerator. Multiply by $d\nu$ and integrate in order to find the energy absorbed from all the Fourier components of the original wave. Then we obtain

$$\int_0^\infty \frac{2\mathrm{A}^2\pi^2\nu\nu_m e^2 h\,d\nu}{(f-4\pi^2\nu^2 m)^2+4\pi^2\nu_m{}^2h^2}=\frac{\mathrm{A}^2e^2}{8\pi m}\left(\frac{\pi}{2}+\tan^{-1}\frac{f}{2\pi\nu_m h}\right),$$

$$=\frac{\mathrm{A}^2e^2}{8m},$$

since f is large compared with $2\pi\nu_m h$. We assume that the intensity of the spectrum of the incident light does not vary rapidly with the wave-length.

If $\mathrm{I}\,d\nu$, as before, represents the energy contained within the range of frequency $d\nu$, which passes through one square centimetre per second,

$$\mathrm{I}=\frac{c\mathrm{A}^2}{8\pi},$$

since $\mathrm{A}^2/8\pi$ is the rate of change of the mean value of the energy per unit volume with frequency. Consequently the energy absorbed per electron per second is

$$\frac{\pi e^2\mathrm{I}}{mc},$$

the same result as was obtained by the other method in (8) above. The free period of vibration of the electrons does not enter into the result. The proof is naturally given in a shortened form here; it will be made clearer by consideration of the passages referred to in Planck's 'Wärmestrahlung.'

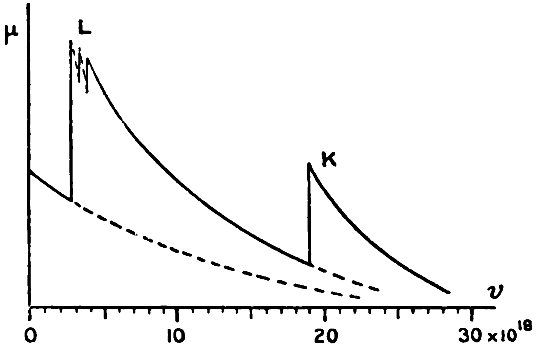
On the one way of deriving the result we assume that the electron starts from rest and that a large number of periods elapse before it loses its energy; as, however, all possible combinations of displacement and velocity may occur, and as the energy increases simply with the time, the initial condition does not affect the result. On the other way, the electron is losing energy uniformly all the time. We cannot prove that the formula holds for the intermediate case—discontinuous losses of energy at short intervals.

Application of the Formula.—The diagram (fig. 1) represents μ as a function of ν for platinum schematically, the K absorption being exaggerated for the sake of a clear diagram.

There are two sharply marked L and K edges from which the absorption gradually falls away in the direction of increasing frequency, and inside the L absorption there are two other edges.

In order to apply formula (4) to calculate p, i. e., the number of electrons per molecule associated with each absorption, it is necessary first to determine $\int\mu d\nu$, i. e., the portion of the area of the curve associated with each absorption. This is not easy. In the first place, the observations at our disposal are not numerous, and it is necessary both to interpolate and exterpolate. Second, it is difficult to know how much of the area to allow to each band. The dotted lines show how I have done this, and there is a certain amount of arbitrariness attaching to the proceeding. Table I. shows the results I have obtained.

Fig. 1.



I have taken the data for Ag, W, Pb, Bi, and the K absorption of Pt and Au from the paper by S. J. M. Allen*, the data for Al from Siegbahn's "The Spectroscopy of X-Rays," the data for Mo from A. H. Compton's "Secondary Radiations produced by X-Rays" (Bulletin of the National Research Council), and the remaining data from the tables in Kaye's "X-Rays." The columns marked "Area" are the areas $\int\mu/\rho d\nu$, where ρ is the density of the material, since the tables give μ/ρ and not μ, and they are in each case a first attempt. The value for Br is obtained from ethyl bromide. The last two columns give the number of electrons per atom worked out by the formula. The mean result for the thirteen K absorptions is 1·03.

---

* Phys. Rev. xxiv. p. 1 (1924).

TABLE I.

Element.	Area.		No. of electrons.	
	K.	L.	K.	L.
Al …………	915×10^{18}		1·52	
Fe …………	303		1·06	
Ni …………	275		1·01	
Cu …………	247		·98	
Zn …………	252		1·02	
Br …………	109		·74	
Mo …………	221		1·32	
Ag …………	248		1·68	
W …………	97		1·11	
Pt …………	75	400×10^{18}	·91	4·8
Au …………	65	390	·79	4·8
Pb …………	55		·71	
Bi …………	39		·51	

This result must be significant. The value of the area varies all the way from 915×10^{18} in the case of Al to 39×10^{18} in the case of Bi, and yet the result comes out approximately constant, showing that we have to deal with a true correlation and not a chance agreement. In the light of the final result the areas might have been apportioned so as to give a much better agreement. There are not enough observations for the L-absorption to state what the 4·8 is an approximation for.

It seems desirable that more measurements should be made of the absorption coefficients, so that the formula may be tested more thoroughly.

Discussion of the Theory.—Theories of the absorption of X-rays have been given from a radically different standpoint*. It is not claimed that the assumption made in this paper of slightly damped electronic oscillators of natural frequencies distributed between the critical absorption frequency and infinity, which are all absorbing energy all the time, constitutes a theory in itself. It is only part of the mechanism. We shall proceed to consider the reasons which lead to this conclusion.

The motion of an electron oscillating about a position of rest may be represented by

$$m\frac{d^2x}{dt^2}+fx=0.$$

---

* L. de Broglie, *Jour. de Phys. et Rad.* iii. p. 33 (1922); *C. R.* clxxi. p. 1137 (1920). H. A. Kramers, Phil. Mag. xlvi. p. 836 (1923).

Owing to its motion the electron will radiate energy; allowing for the back pressure of the radiation in the equation, we obtain

$$m\frac{d^2x}{dt^2}-\frac{2}{3}\frac{e^2}{c^3}\frac{d^3x}{dt^3}+fx=0.$$

If the frequency is ν, this may be written

$$m\frac{d^2x}{dt^2}+\frac{2e^2}{3c^3}(2\pi\nu)^2\frac{dx}{dt}+fx=0.$$

So the equation has the same form as the left-hand side of (2), if

$$h=\frac{2e^2}{3c^3}(2\pi\nu)^2.$$

Let us assume that $x=l\sin 2\pi\nu t$.

Then the rate at which energy is being radiated is

$$h\left(\frac{dx}{dt}\right)^2=hl^2(2\pi\nu)^2\cos^2 2\pi\nu t,$$

the mean value of which is $2hl^2\pi^2\nu^2$. On substituting for h the energy radiated in one-half period is

$$\frac{8}{3}\frac{\pi^4\nu^3e^2l^2}{c^3}.$$

The maximum value of the kinetic energy is

$$\tfrac{1}{2}ml^2(2\pi\nu)^2.$$

So the fraction of the energy radiated in one-half period is

$$\frac{4}{3}\frac{\pi^2e^2\nu}{mc^3}=1\cdot2\times10^{-22}\nu.$$

Hence the rate of decay of the energy of the electron may be represented by

$$\exp.(-2\cdot4\times10^{-22}\nu^2t).$$

If the frequency is that of Na light, the energy falls to one-tenth of its value in $3\cdot8\times10^{-8}$ sec. For the case of X-rays of wave-length 1 Å.U., the energy is lost $3\cdot6\times10^7$ times as fast.

According to (3) the rate at which an electron absorbs energy is

$$\frac{\pi e^2\mathrm{I}}{mc}=\cdot0262\mathrm{I}.$$

Suppose that the frequency of the electron is in the visible spectrum, and that it is exposed to an illumination of 1 metre-candle. The energy received by a surface at a distance of one metre from a Hefner lamp is $2{\cdot}15\times10^{-5}$ gm. cals. per sq. cm. per sec. About 1 per cent. of this is radiated as light. The difference in frequency between the ends of the visible spectrum is $3{\cdot}75\times10^{14}$. Consequently, taking the average value for the visible spectrum,

$$I=\frac{2{\cdot}15\times10^{-7}\times42\times10^{6}}{3{\cdot}75\times10^{14}}=2{\cdot}41\times10^{-14},$$

and the energy absorbed per second is

$$\cdot0262\times2{\cdot}41\times10^{-14}=6{\cdot}35\times10^{-16}\text{ erg.}$$

If we take $3{\cdot}6\times10^{-12}$ as the average value of the quantum for the visible spectrum, the time required to absorb one quantum is about 157 hours. The time required to lose nine-tenths of a quantum is only $3{\cdot}8\times10^{-8}$ sec. Clearly the balance between emission and absorption takes place at a very small fraction of the quantum. Let us denote this fraction by x. Then its value is obtained from the following equation

$$6{\cdot}35\times10^{-16}=x3{\cdot}6\times10^{-12}\times2{\cdot}4\times10^{-22}\nu^{2},$$

which gives $x=2{\cdot}43\times10^{-12}$.

Thus, if the electron were exposed to the light-wave its energy would gradually increase and the radiation loss would simultaneously increase, until the energy reached a value somewhat greater than one-billionth of a quantum. Beyond this there would be no increase. The chances of the electron acquiring a quantum of energy must be much worse in the X-ray spectrum, since both the quantum and the radiation loss are much larger in that region.

But we know that the photo-electrons excited by X-rays have one quantum of energy. The energy must therefore be taken from the absorbing electron and transferred to some other system, while the radiation loss from the former is still a long way below its rate of absorption, and must pass from this other system to the photo-electron.

We thus arrive at the escapement theory of Sir Joseph Larmor *. He regards the electronic radiator as analogous to the pendulum of a clock driven by the energy of a coiled spring which is fed into the motion by an escapement, only his model is reversible; the pendulum may feed its energy

---

* Phil. Mag. xlii. p. 592 (1921).

back through the escapement into the spring. This analogy applies to our problems well.

The question arises as to the extent of spectrum from which each electron absorbs its energy. Let us go back to equation (2)

$$m\frac{d^2x}{dt^2}+h\frac{dx}{dt}+fx=-eX,$$

assume that we are dealing with one free period, and define the breadth of the band in the absorption spectrum as the difference between the wave-lengths for which the coefficient of absorption has half its maximum value. Then it may be shown (*cf.* my book on 'Light,' p. 433), that this is equal to

$$\frac{h\lambda^2}{2m\pi c}.$$

If we assume that the loss of energy is wholly a radiation loss and substitute the appropriate value of h, this becomes

$$\frac{4\pi}{3}\frac{e^2}{mc^2},$$

the numerical value of which is $1{\cdot}16\times10^{-4}$ Å.U. This is a breadth much too small to observe.

Now we know that the radiation loss is only part of the loss. The "h" must cover in addition the removal of energy by the "escapement." Hence its value must be greater than the figure we have assumed, but not very much greater, and consequently the bands, broader than the breadth we have arrived at, but not much broader.

To conclude: the picture at which we arrive at is this. If we take, for example, the case of Fe, within the region of the K absorption, 25 of its 26 electrons are taking energy from the incident rays and "scattering" it, losing it by resonance radiation. The remaining electron absorbs energy from a narrow region somewhere between the head of the band and infinite frequency; it scatters a small proportion of this energy but transmits most to another system of which we know nothing. Its own energy never becomes more than an insignificant fraction of the appropriate quantum. Outside this limited region the remaining electron "scatters" as well as the others.

April 2, 1926.

XLIV. *The Magnetic Stability of Permanent Magnets.*

By ROBERT COCHRAN GRAY, *M.A.*, *D.Sc.*[*]

Introductory.

A PIECE of steel, after magnetization, experiences a gradual loss of magnetism, the rate of loss tending to zero only after the lapse of several months. The process of *ageing*, either by heat treatment, vibration, or partial demagnetization, or by all of these, represents an attempt to bring the magnet into its final stable state in a few hours instead of months. This paper gives the effect of each of these treatments on the magnetic stability of a magnet.

Mechanical Stability and Magnetic Stability.

It is important to distinguish carefully between *mechanical stability* and *magnetic stability.* Strains in the material gradually disappear, and partial recrystallization takes place, altering the nature of the material; and during these changes, and because of them, the magnetic quality alters. This mechanical stabilization should be complete before the material is magnetized. In magnetic stabilization the principle is that of subjecting the magnet, before use, to a treatment equivalent to that which it will experience when in use. How the nature of this experience may be evaluated will be indicated later. This paper refers to materials already mechanically stable; such materials were available for test in the form of cylindrical magnets that had been in use in a first-year students' laboratory for from ten to forty years.

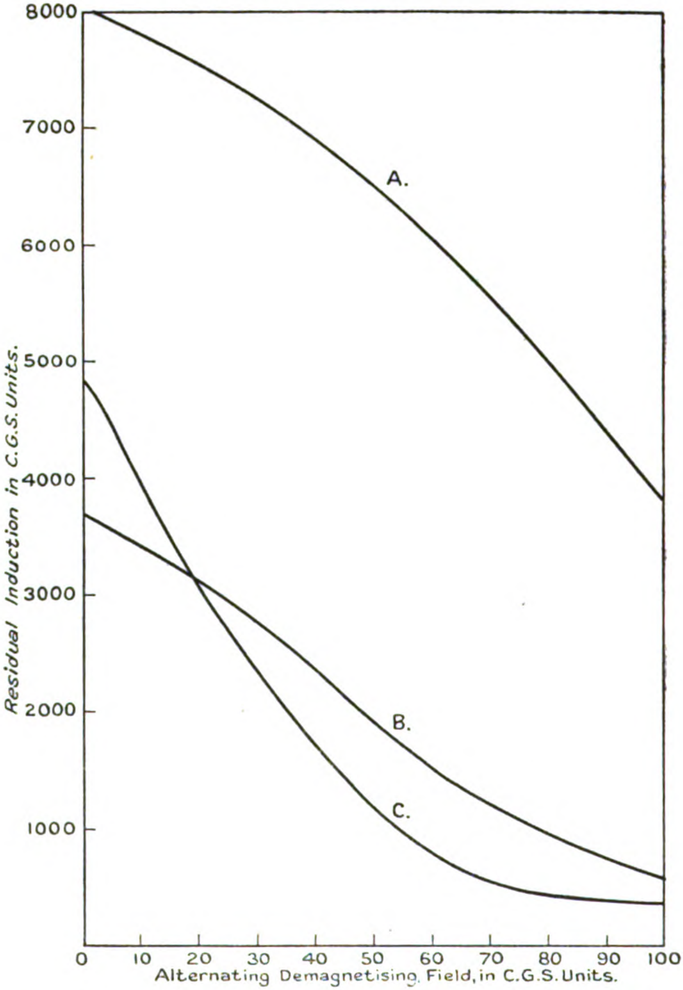
Effect of Demagnetization.

The only safe method of demagnetization is to subject the magnet to an alternating field, beginning at a definite value to be here called the *demagnetizing field*, and to reduce this gradually to zero. If we magnetize a specimen to saturation, and then apply a small demagnetizing field in this way, we remove a small amount of the magnetism; each successive increase in the demagnetizing field (see fig. 1) causes an additional loss. The greatest loss of magnetism for a given small increase in the demagnetizing field occurs when the demagnetizing field is slightly less than the saturation coercive force (H_{cs}) of the material. The figure gives the curves obtained from three materials A, B, C, of coercive force 113, 60, 34 respectively. Material A was permanite. The application of a demagnetizing field equal to the coercive force of the material results in a reduction of the residual induction by over 50 per cent., and near this field the curve is steepest. Thus, it is most important that material for permanent magnets should have, in addition to a high residual

---

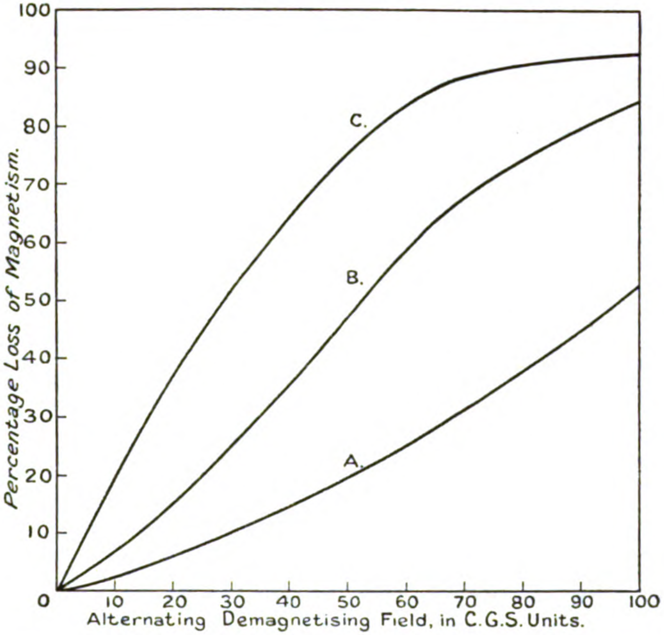
[*] Communicated by the Author.

Fig. 1.—Showing decrease in magnetism for various alternating demagnetizing fields. Materials A, B, C had coercive force 113, 60, 34 units respectively.



induction, as high a coercive force as possible. The percentage loss of magnetism for different demagnetizing fields is given in fig. 2, where the effect of high coercive force in keeping down the loss is more apparent. For example, a demagnetizing field of 50 units reduces the residual induction by 19, 48, 75 per cent., for the materials of coercive force 113, 60, 34 units respectively. Further, it is quite possible that a material of high coercive force and comparatively low residual induction may possess, when stabilized by the proper demagnetizing field, a larger amount of magnetism than a material of much higher residual induction but of lower coercive force. Reference to fig. 1 will show that material B, of initial residual induction only 75 per cent. of that of material C, retains after the application of fields greater than 20 units more magnetism than material C; this effect is due to the higher coercive force possessed by material B. Such material of higher coercive force will be less affected in practice in the

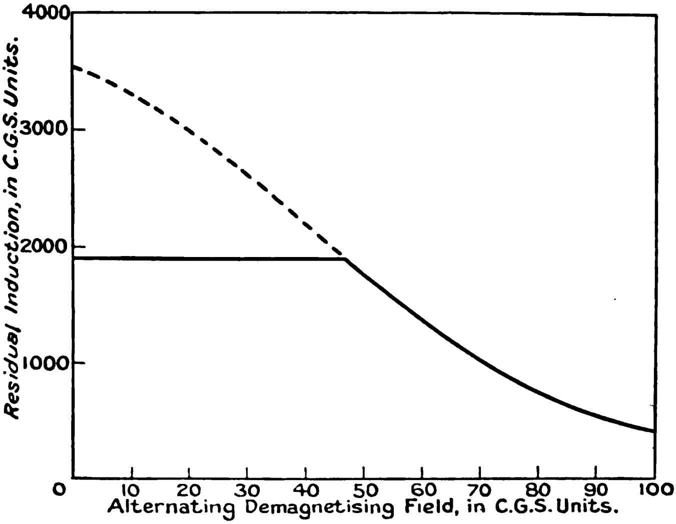
Fig. 2.—Showing percentage loss of magnetism for various alternating demagnetizing fields.



event of its experiencing larger demagnetizing fields than had been expected ; this is indicated by the smaller gradient, for moderate fields, of the curve of B compared with the gradient of the curve of C.

If a demagnetizing field of, say, 50 units has been applied to a magnet, no subsequent demagnetizing field of amount less than 50 units will have any effect on the magnetism. On this fact is based the method of magnetic stabilization by partial demagnetization. The *stabilizing field*, i. e. the initial value of the demagnetizing field, should be that likely to be experienced by the magnet when in use. The demagnetization curve is then of the type shown in fig. 3, where the stabilizing field is 47 units. The first portion of the curve is horizontal, representing magnetic stability ; the remainder of the curve beyond the stabilizing field follows the original curve.

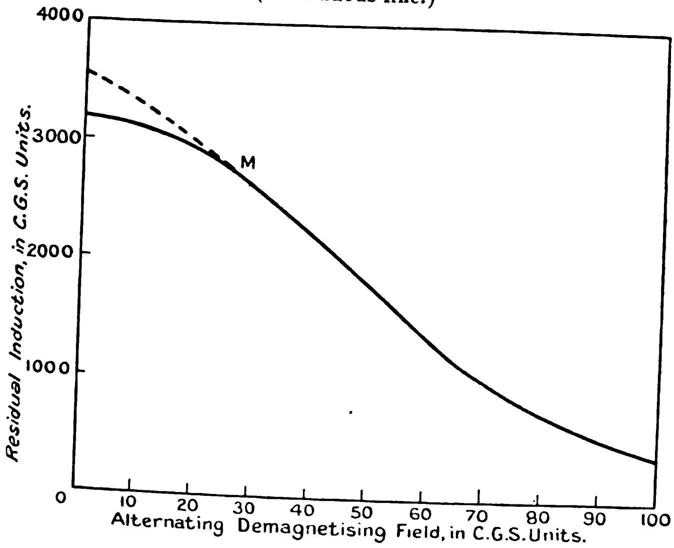
Fig. 3.—Showing the magnetic stability due to partial demagnetization by an alternating field of 47 units. (Continuous line.)



Effect of Steaming.

Stabilization against variations of temperature consists of keeping the specimen at 100° C. for an hour, then at room temperature for an hour, and continuing this alternation until the magnetism attains a steady state, usually after three or four such cycles. The changes in volume, and slight softening, alter the fields controlling the elemental magnets, with the result that part of the residual induction disappears. When there is taken a demagnetization curve of a specimen stabilized in this way, we find that small demagnetizing fields have a small but appreciable effect (see fig. 4); this effect remains small until a definite field M is reached, after which the effects are large and the curve follows the usual run. For the specimen whose curve is given in fig. 4, this

Fig. 4.—Showing the effect of steaming a magnet. (Continuous line.)

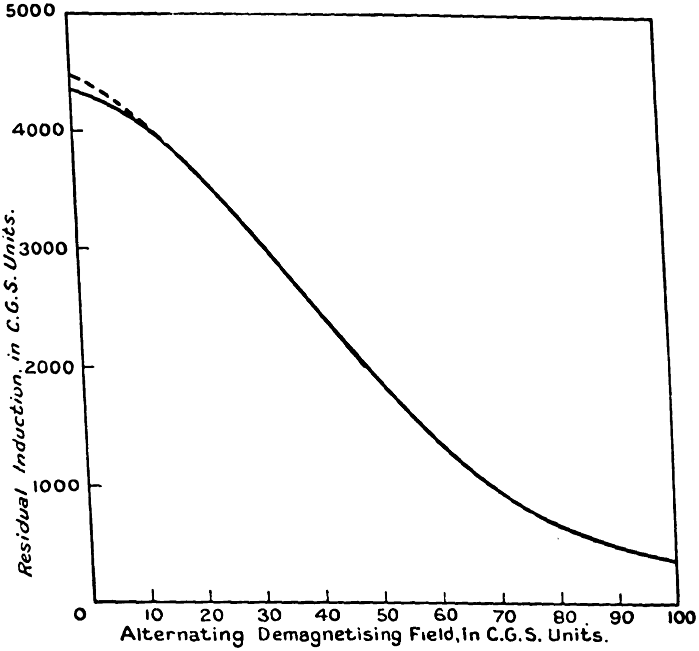


field M was about 29 units. The important point here is that if the material, before steaming, is demagnetized by a field greater than M, steaming has no effect: the partial demagnetization has stabilized the material against variations of temperature.

Effect of Vibration.

The effect of vibration on the magnetism of a specimen is very similar to that of steaming. A rod was magnetized, then dropped fifty times, on alternate ends, a height of one foot, on to a stone floor, and caught on the rebound. The demagnetization curve is shown in fig. 5; it will be seen that the curve joins the original curve at a field of about 12 units. When the material was initially demagnetized by a field greater than this, vibration had no effect. Thus stabilization against vibration, like stabilization against small variations in temperature, may be carried out most easily by demagnetization by a suitable field.

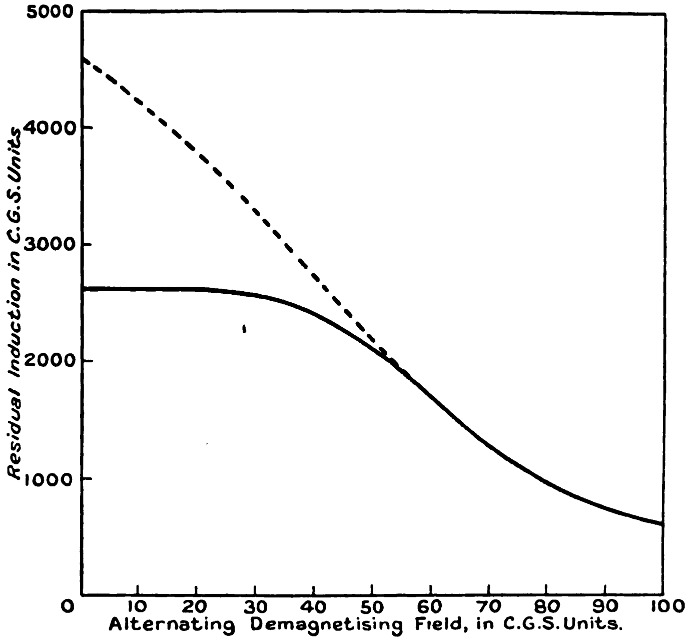
Fig. 5.—Showing the effect of vibrating a magnet. (Continuous line.)



Effect of Time.

All the specimens, except the permanite, used in these tests had been magnetized some years ago, and each had lost a proportion of its original magnetism. The demagnetization curve of a typical specimen in this "naturally aged" state is shown in fig. 6. It will be seen that for this specimen the curve meets the main curve, which was taken after subsequent re-magnetization, at a field of about 53 units. This field lay, in every case, between 52 and 57 units, the average being 55, which is the equivalent therefore of the demagnetizing treatment experienced in practice by an ordinary binnacle magnet treated with little care. But while this "field of experience" was nearly constant, the percentage loss of magnetism varied within the wide limits of 35 and 60 per cent. It is interesting to note that the permanite specimen, magnetized by the makers, and stabilized partly by them, presumably, and partly by two years' use, showed a field of experience of 54 units and a percentage loss of 20 per cent. Comparison of the loss and the coercive force in all these cases showed that the law that "the percentage loss is inversely proportional to the coercive force"

Fig. 6.—Showing the effect of time on a magnet. (Continuous line.)

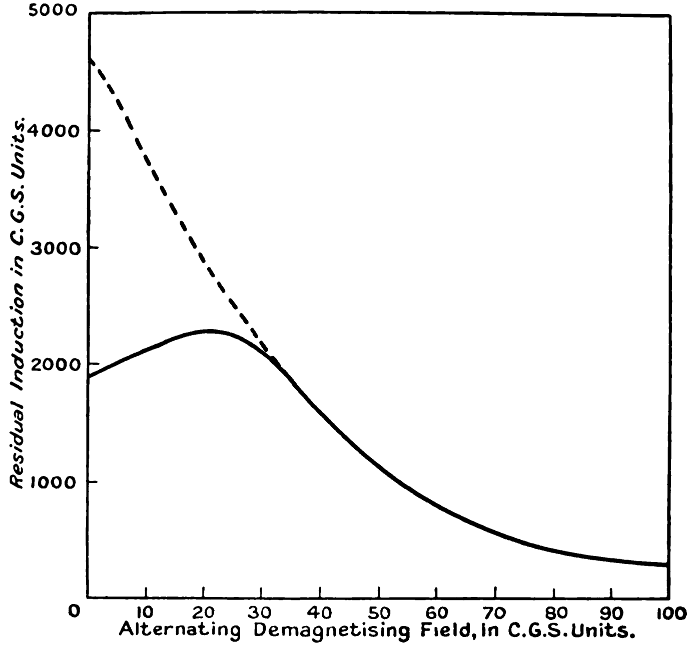


is approximately true within the conditions covered by these tests; if this law held for a coercive force of 225 units, we should expect a loss of magnetism of only 10 per cent. after the lapse of years. The rule in magnetic stabilization should therefore be partial demagnetization by a definite field, rather than the removal of a definite percentage of the residual induction. It is extremely probable that our specimens, if magnetized to saturation and then demagnetized by a field of 55 units, would show no appreciable loss of magnetism with time

Effect of Partial Magnetization in the Opposite Sense.

It might be expected that the reduction in magnetism that is necessary for stabilization might most easily be effected by applying a field, of properly chosen amount, in the opposite direction to the original magnetizing field. This method cannot be recommended. Fig. 7 gives the demagnetization curve of a specimen that had been magnetized in one direction by a field of 280 units and had then been exposed to a field of 34 units in the opposite direction. It will be noticed, apart from the peculiarity that for low fields the process of "demagnetization" actually increases the magnetism of the specimen, that the magnetism is affected even by small demagnetizing fields. A comparison of figs. 3 and 7 will show the decided advantage in stability attained by partial demagnetization by means of an alternating decreasing field.

Fig. 7.—Showing the effect of applying a weak field to a magnet, in the direction opposite to the original magnetization.



Conclusion.

It has been mentioned that these rod magnets had experienced, when in use, demagnetizing fields averaging 55 units.

One of these magnets partially demagnetized by a field of 29 units was unaffected by steaming; another, partially demagnetized by a field of 12 units, was unaffected by moderate vibration. Hence for complete magnetic stability of these magnets it is necessary and sufficient that a demagnetizing field of 55 units should be applied. Steaming and vibration are probably necessary in order to stabilize the material mechanically, and thus will affect indirectly the magnetic constants (*e. g.* coercive force); but they have no direct use in magnetic stabilization after mechanical stabilization, since their effect is more than covered by the partial demagnetization necessary to render the material immune to the effects of the demagnetizing fields likely to be experienced by the magnet when in use.

Summary.

A distinction is made between the stabilization of the *material* intended for permanent magnets, and the stabilization of its *magnetism*. After the material has been mechanically stabilized, it should be magnetized to saturation and then demagnetized by an alternating decreasing field whose maximum value is slightly above that of the field likely to be experienced when the magnet is in use. A method of finding the value of this latter field is given. This partial demagnetization stabilizes the magnet not only against demagnetizing fields, but also against temperature variations and against moderate vibration. The importance of a high coercive force is indicated; the percentage loss of magnetism with time is, approximately, inversely proportional to the coercive force.

XLV. *Absorption and Resonance Radiation in Excited Helium and the Structure of the* 3889 *Line.* *By* W. H. McCurdy, *Ph.D., National Research Council Fellow in Physics* [*].

[Plate IX.]

INTRODUCTION.

PASCHEN [†] observed that a column of weakly excited helium showed marked absorbing power for light of wave-length equal to that of the first term of the principal series of both systems of the helium spectrum, 10830 Å and 20852 Å respectively. Further, that resonance radiation of wave-length 10830 Å was produced in the weakly excited gas by the monochromatic radiation of that wave-length from a second helium discharge tube. Absorption of light of wave-length corresponding to transitions from other than the normal state of the atoms involved has been frequently observed. Ladenburg[*] and others have observed marked absorption of the Balmer series in a strong discharge in hydrogen. Compton and Turner[†] have observed absorption of several lines of which the initial state in absorption is $2p$ and the final a higher s state.

---

[*] Communicated by the Author.

[†] Paschen, *Ann. d. Phys.* xlv. p. 625 (1914).

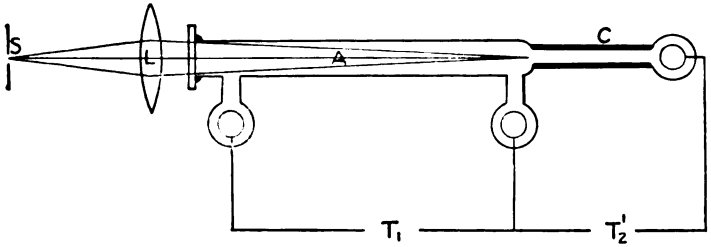
More recently Meissner[‡] has made a more detailed study of the absorption in weakly excited neon. He has observed absorption of twenty-six lines having initial states in absorption $2s_i$, where i varies from 2 to 5 inclusive. He has not observed any absorption for lines of which the initial state is a p level.

The following is a report of an investigation of a more general nature of the optical properties of excited helium. The absorption of most of the helium lines between 6678 Å and 3614 Å has been investigated, and photographs showing the existence of resonance radiation of wave-length 3889 Å have been obtained.

Method.

The arrangement of apparatus used in the work is shown diagrammatically in fig. 1. The capillary C served as source of light, and the larger part of the tube A served as the absorbing column, which was about 80 cm. in length.

Fig. 1.



---

[*] Ladenburg, *Verh. d. Deutsch. Phys. Ges.* x. p. 580 (1908), & xii. p. 54 (1910); also Kimura and Nakamura, Jap. Journ. of Phys. ii. p. 53 (1923), and Hulbert, Phys. Rev. xxvi. p. 124 (1925).

[†] Compton and Turner, Phys. Rev. xxv. p. 606 (1925).

[‡] Meissner, *Ann. d. Phys.* lxxvi. p. 124 (1925).

The two portions of the tube could be excited independently by means of the two transformers T_1, T_2' giving 6000 to 10,000 volts on the secondary, with 120 volts 60 cycle A.C. on the primary. The current in either tube could be varied at will by means of a resistance in series with the primary of the transformer without appreciably influencing the other. The electrodes were of aluminium foil and were freed from hydrogen by running a discharge for some time before introducing the helium. The helium used was stored over water and dried by phosphorus pentoxide and purified by standing for some time in charcoal immersed in liquid air. No trace of hydrogen could be observed visually in examination of the tube spectrum.

The end of the capillary C was focussed on the slit of the spectrograph S by means of the lens L placed as near the end of the tube as possible, thus eliminating the radiation from the absorbing column as much as possible. It is, of course, impossible to eliminate this completely, but the above arrangement appeared satisfactory. The observing system consisted of a glass echelon grating of twenty steps each of thickness about 6 mm. A glass prism of about 7 cm. base was used to separate the lines. In making the photographs, a four-foot photographic objective was used and Hammer rapid plates for the spectral region in which they are sensitive.

The object of using this method was to avoid the necessity of making photometric determinations of the density of the plates obtained, since the absorption appeared as the reversal of the line observed. As an indication of the degree of absorption the width of the reversal was observed. This method would of course not be satisfactory for detailed or accurate investigation, since the maximum width of the reversed portion of the line is equal to the width of the emission line in the absorbing column, which is probably less than that of the line from the capillary due to the lower temperature of the absorbing column and also to the lower field strengths in the larger absorbing tube. This, however, is probably sufficient for the approximate results desired, especially since no extreme care was taken to eliminate all impurities from the helium, which obviously detracts from the theoretical values of the results. All that can be said is that there was not sufficient impurity present to show spectroscopically, in visual observations.

A series of exposures of equal times were made on one plate with gradually increasing current in the absorbing column, starting from zero. By this method the effect of the current in the absorbing column was quickly and easily determined. The process was repeated for most of the lines between 6678 Å and 3614 Å and for pressures of helium between 9·8 mm. and 0·8 mm. Owing to the fact that it was impossible to eliminate completely the glow in the absorbing column with this arrangement of apparatus, it was never possible to obtain a photograph of the unreversed 3889 line.

RESULTS.

It was found that not only the 1S—mP and $1\sigma - m\pi$ series, but also the 1P—mD and $1\pi - m\delta$ showed strong absorption. It was found impossible, however, to detect any trace of absorption in the case of the 1P—mS or $1\pi - m\sigma$ series. Table I. has been prepared showing the results that were obtained at a pressure of 4 mm. The amount of the absorption is estimated from the width of the reversal of the line as already indicated.

TABLE I.

Absorption of the helium lines in a column of helium of length about 80 cm. excited by A. C. Current density of the exciting current about 100 m. amps. per cm². Pressure of the helium 4 mm.

Wave-length.	Line.	Absorption.
6678 Å.	1P—2D	Weak (only under extreme conditions).
4922	1P—3D	Very weak (only under extreme conditions).
4387	1P—4D	Not detectable.
5016	1S—2P	Strong.
3964	1S—3P	Weak.
3614	1S—4P	Very weak.
3889	$1\sigma-2\pi$	Very strong.
3187	$1\sigma-3\pi$	Strong.
5876	$1\pi-2\delta$	Strong.
4471	$1\pi-3\delta$	Fair.
4026	$1\pi-4\delta$	Weak.
3819	$1\pi-5\delta$	Very weak.

No absorption was to be found for any other lines in the region considered etween 6678 and 3187 Å.

It will be observed that the principal series of both systems shows a greater absorption for corresponding terms than does the subordinate series. This is to be expected, since the principal series are stronger in emission than are the subordinate series. It is also to be expected that the $1P-mS$ and $1\pi-m\sigma$ series should show little absorption since they are comparatively weak in emission. The result shows very clearly, however, that there are two factors involved in the consideration of the emission and absorption spectra of gases. Since both subordinate series have the same initial state, the number of the atoms in a state to absorb the two series is the same. Still the one series shows strong absorption while the other shows none. Thus the factor involving the probability of a given transition must play fully as important a rôle as the concentration of atoms in a state initial to the transition considered. This is still further emphasized by the results on different lines of a given series.

Effect of Excitation on the observed Absorption.—Figs. 1, 2, 3, 4, 5, and 6 (Pl. IX.) show the absorption of different lines under different pressure conditions. Diagrams *a* to *d* are taken with increasing current in the absorbing column. It is apparent that the width of the reversal of the line increases with the current in the absorbing column. At high current densities in the absorbing column, however, the width of the reversal appears to decrease. This is probably due to the contribution of the absorbing column to the observed radiation. If this could be entirely eliminated, it is probable that the width of the reversal would increase with the excitation of the absorption tube until the state was reached where the reversal was equal in width to the emission line of the absorbing column. The results show, however, a marked increase in the absorption with an increase in the excitation of the absorbing column.

Absorption of Series.—In the case of the $1S-mP$ series Paschen * observed absorption of the first term of the series. The present investigation has shown observable absorption to the fourth term 3614 Å. The width of the reversal is found to fall off rapidly as the higher terms of the series are studied. In reproducing the results in enlargements only the second and third terms have been used. Comparing this with the observed reversal of the $1P-mD$ series, it was found that reversal could be observed only to the second term, and only with intense excitation in the absorbing column. Observations on these were made visually since the first term is in the red, 6678, which require the use of red sensitive plates. Thus it appears that the rate at which the absorption falls off is less for the principal than for the subordinate series. The same would probably be true in the case of the doublet system also if observations were sufficiently extensive. In fig. 5 (Pl. IX.) is shown the reversal of the 3964 Å line under conditions comparable with those under which the results on the 5016 Å line shown in fig. 3 were obtained. Fig. 6 shows the reversal of the yellow line 5876 Å, but it is not comparable with the photographs of the 3889 Å line shown in figs. 2 and 4 (Pl. IX.). In the case of the doublet system observations showed absorption to the fourth term of the subordinate series while, up to the present at least, observations have been made only on terms up to the third of the principal series, so no conclusions can be drawn from the comparison of the results on the two series.

---

* Paschen, *loc. cit.*

Effect of Pressure.—Figs. 1 and 2 (Pl. IX.) show the reversal of the corresponding lines of the two systems 5016 Å and 3889 Å respectively at 9·8 mm. pressure, and figs. 3 and 4 the same at ·8 mm. pressure. Though the enlargements do not show the results as distinctly as the original plates, still it may be observed that the reversal in the case of the line 3889 Å is wider at the higher pressure while the reverse is true of the line 5016 Å. Thus it appears that the pressure has a great effect on the absorption of the different series. It is as should be expected from the emission spectra of the gas under different pressures. At high pressures the doublet system is predominant, giving the discharge a distinctly yellow colour, while at low pressures the singlet system predominates and the discharge has a greenish tinge. Thus it is to be expected that the singlets will be absorbed more strongly at low pressures and the doublets more strongly at high pressures.

As was stated in the preceding paragraph it was possible to reproduce the reversal of the 3964 Å line only at low pressures. A similar result was obtained in the case of the doublet system, in which it was found that the absorption appeared to fall off more rapidly at low pressures than at higher ones. Detailed investigation of this sort, however, would be justified only with the use of very pure helium and under conditions more reproducible than is possible using transformer excitation and ordinary purification processes.

Effects of Impurities.—The effect of hydrogen on the absorption is clearly shown by comparison of figs. 4 and 7 (Pl. IX.)

Fig. 7 (Pl. IX.) shows the reversal of the 3889 Å line when the spectrum of the discharge showed the Balmer lines of hydrogen distinctly, while fig. 4 shows the reversal of the same line under similar pressure in helium, pure enough to render the Balmer lines invisible. It is apparent that hydrogen greatly reduces the absorption. This is in agreement with the results obtained by Paschen * and Meisner†.

The effect of the impurity is probably a reduction of the life of an excited atom. The assumption that this was the case was made recently in considering the cause of striations in the positive column of a discharge ‡, and this appears to be a partial confirmation of that hypothesis. In this case the excited atom of helium contains sufficient energy to ionize the hydrogen in collisions of the second kind.

STRUCTURE OF THE 3889 LINE.

Examination of the photographs of the reversed 3889 line showed that the reversal was not symmetrical, indicating an unresolved component on the short wave-length side of the line. It was thus decided to look for another component to the line. For this work a quartz Lummer-Gehrcke plate was used and the tube which served as the source of light was cooled by wrapping it with cotton which was kept wet with liquid air. This, together with a very low current in the tube, produced a line much narrower than was observed in the absorption experiments.

An enlarged photograph of the fringes produced by the line is shown in fig. 9 (Pl. IX.). This shows, as was expected, that there is a weak component on the short wave-length side of the line. The separation of this component from the main component of the line as calculated from the dimensions of the plate was found to be ·044 Å. This was checked by use of a second plate of different dimensions. Thus assuming the wave-length of the line as given in the tables to be that of the strong component, the wave-length of the weak component comes out to be 3888·602 Å.

RESONANCE RADIATION IN THE WEAKLY EXCITED HELIUM.

The extremely strong absorption in the excited helium of the 3889 Å line indicated the possibility of detecting resonance radiation of this wave-length, if the weakly

---

* Paschen, *loc. cit.* † Meissner, *loc. cit.*

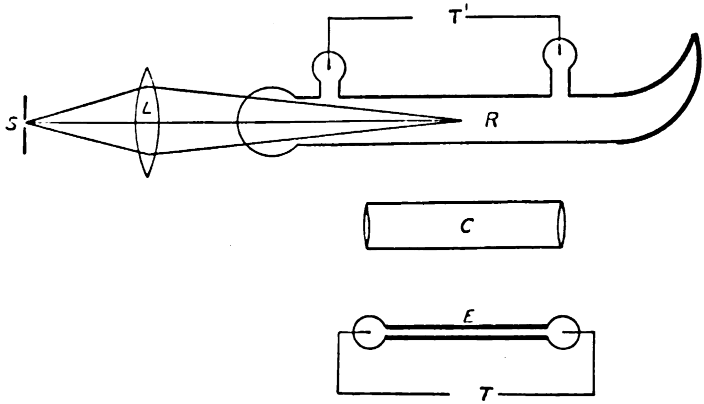
‡ McCurdy, Phil. Mag. xlviii. p. 898 (1924).

excited gas was subjected to strong monochromatic radiation of this light. Paschen observed resonance of the first line of this series by means of a thermopile and it was considered worth while to attempt to photograph resonance of the second line.

Method.

The method used needs little description. The apparatus is shown diagrammatically in fig. 2. The capillary tube E. filled with helium to about 4 mm. pressure served as a source of monochromatic radiation, while the tube R, filled to 3·6 mm. pressure, served as resonance tube. The two tubes were excited by means of transformers as in the previous work on absorption.

Fig. 2.



The light from the capillary E was focussed along the axis of the resonance tube R by means of the cylindrical lens C. The radiation from the resonance tube was focussed on the wide slit of a small quartz spectrograph S by means of the lens L, placed at a considerable distance from the tube in order that as much of the length of the tube as possible should contribute to the observed radiation. In order to eliminate, as far as possible, light reflected from the sides of the tube, the end was drawn off as shown and painted black. Since the light from the emission tube was focussed along the axis of the resonance tube, any resonance radiation should be observed as an increase in the intensity of the light from the central portion of the tube.

In making the observations, three exposures of equal time were made on a single plate. Thus no errors were introduced in the process of developing. The first exposure was made with a weak discharge flowing in the resonance tube and the light from the capillary screened off by placing a black screen between the two tubes. This exposure gave the intensity of the radiation due to the electrical excitation of the resonance tube. The second exposure was taken with the same current flowing in the resonance tube but with the screen removed. Thus the radiation observed in this case consisted of that due to electrical excitation and also that due to the resonance produced by the light from the emission tube E. A third exposure was made with no current flowing in the resonance tube but with the emission tube running and the screen removed. This would prove whether or not there was an appreciable amount of scattered light from the emission tube reaching the spectrograph.

Results.

Fig. 8 (Pl. IX.) shows the results of the experiments. It was found that no trace of scattered light was to be observed on the plates. The exposures were of only 90 seconds and the scattered light was not of sufficient intensity to be observed. The results show, however, a distinct increase in the intensity of the light when the radiation from the tube E is incident on the resonance tube. This must be due to resonance produced by the light of the same wave-length, 3889 Å, from the emission tube. In fig. 8, *a* is the 3889 line of the resonance tube alone and *b* is with the screen removed. The central portion of the line in fig. 8 *b* is seen to be increased in intensity in comparison with fig. 8 *a*.

Visual observations were made on the green line, 5016 Å, but it was found that no apparent increase occurred under the action of the light from the tube E. It is possible that observation of resonance radiation of this wave-length may be successful under more favourable conditions. These should consist of very low pressure and extremely pure helium, in order that the absorption for this light may be very strong. It is very probable that resonance radiation of wave-length 3187 Å would have been detected had the apparatus used been of quartz, but is was not considered advisable to construct tubes of quartz for the work.

SUMMARY.

Results of these experiments on the optical properties of excited helium may be summarized as follows:—

(1) Excited helium shows marked absorption for terms of both the principal and diffuse subordinate series of the two systems of the helium spectrum.

(2) Resonance radiation of wave-length 3889 A has been observed in the weakly excited gas under the influence of monochromatic radiation of this wave-length.

(3) Examination of the structure of the 3889 line of helium has shown it to be a doublet in agreement with the rest of the spectral system. The second component is weak and of wave-length 0·044 A less than the main component.

In conclusion the author wishes to express his thanks to Prof. R. W. Wood for his suggestions throughout the work, and also to the National Research Council for the award of a Fellowship which made the investigation possible.

Johns Hopkins University,
Baltimore, Md.,
February 20th, 1926.

XLVI. *On the Determination of the Velocity Constant of a Unimolecular Reaction.* *By* E. A. GUGGENHEIM, *Wollaston Student, Gonville and Caius College, Cambridge**.

THE rate of a chemical reaction is frequently determined by observation of some physical property of the system, whose value is a linear function of the concentration of a reacting substance. In the case of a unimolecular reaction, whether reversible or irreversible, if v is the "reading" at time t and if v_0 and v_∞ are the initial $(t=0)$ and final $(t=\infty)$ readings, then the relation between v and t is

$$v_\infty - v = (v_\infty - v_0)e^{-kt} \quad . \quad . \quad . \quad . \quad (1.1)$$

or

$$\log_e \frac{v_\infty - v}{v_\infty - v_0} + kt = 0, \quad . \quad . \quad . \quad . \quad (1.2)$$

where k is the velocity constant (in the case of a reversible reaction k is the sum of the constants of the two opposed processes). For the sake of definiteness we shall assume that v increases with t; if this is not the case it is only necessary to replace v by $-v$, v_0 by $-v_0$, and v_∞ by $-v_\infty$. We shall thus treat $v_\infty - v$ as essentially positive.

---

* Communicated by Prof. R. H. Fowler, F.R.S., Cambridge.

To determine the value of k it is usual to plot $\log(v_\infty - v)$ against t and measure the slope of the straight line so obtained. Other commonly used methods of treatment, such as calculating k from v_∞ and various pairs of values of v and then averaging the values of k so obtained, are substantially equivalent to the above. They are all alike in giving to v_∞ a weight at least approximately equal to the sum of the weights given to all the other readings, and an error of $+\epsilon$ in v_∞ affects the value obtained for k in the same way as a systematic error of $-\epsilon$ (in the same direction) in all the other readings. This treatment is justifiable only if v_∞ is known with appreciably greater accuracy than the other v's. This may be so if the final value is observed over a long period after the reaction has practically reached completion. If this is ever carried out in practice, it is the exception rather than the rule.

Not infrequently it is inconvenient or even impossible to observe the end-point directly at all; in such cases it is usual to obtain a value for it by extrapolation. If this is done by any straightforward method the value of v_∞ so obtained will at the best be no more accurate than any of the directly observed values of v. The best value for k will then not be obtained by any of the usual methods which give great weight to v_∞.

Equation (1.1) or (1.2) regarded as that of a v–t curve contains three parameters, k, v_0, and v_∞; hence three points (v_1, t_1), (v_2, t_2), (v_3, t_3) are theoretically sufficient to fix the curve and so determine the values of all three parameters. In a recent paper in this journal * Mr. R. Christie Smith has shown that if the three points be so chosen that the time-interval $(t_2 - t_1)$ between the former pair is equal to that $(t_3 - t_2)$ between the latter pair, then it is easy to eliminate k and v_0 and so obtain v_∞ as an explicit function of v_1, v_2, v_3. The equation obtained becomes in our notation

$$v_\infty = v_1 + \frac{(v_2 - v_1)^2}{2v_2 - v_1 - v_3}. \quad . \quad . \quad . \quad . \quad (2)$$

If the values of v_1, v_2, v_3 were known exactly this would be a neat way of evaluating v_∞. Actually, owing to the inevitable inaccuracies of the individual readings, it would be essential to apply the process to a large number of such sets of three points and then average somehow: it is not easy to see how this is to be done giving equal weights to all the observed readings. Failing this, the value obtained could not satisfy the criterion of being more accurate than

---

* Phil. Mag. vol. i. (Feb. 1926).

any of the other readings, and so would not be suitable for the ordinary method of plotting.

In any case it would seem a more natural procedure, instead of eliminating k and v, to eliminate v_0 and v_∞, so obtaining directly for k the very simple formula

$$k = \frac{1}{\Delta t} \log_e \frac{v_2 - v_1}{v_3 - v_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\Delta t = t_2 - t_1 = t_3 - t_2$.

The following treatment is in principle somewhat similar to this, but is more convenient in practice.

Suppose $v_1, \ldots v_i, \ldots v_n$ are n readings taken at times $t_1, \ldots t_i, \ldots t_n$ (without any restriction as to the intervals), and that n more readings, $v_1', \ldots v_i', \ldots v_n'$, be taken at times $t_1 + \tau, \ldots t_i + \tau, \ldots t_n + \tau$ each a constant time τ after one of the previous set. Then we have the equations

$$v_\infty - v_i = (v_\infty - v_0) e^{-kt_i}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

$$v_\infty - v_i' = (v_\infty - v_0) e^{-kt_i - k\tau}. \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

By subtraction

$$v_i' - v_i = (v_\infty - v_0)(1 - e^{-k\tau}) e^{-kt_i}, \quad . \quad . \quad (4.3)$$

or taking logarithms,

$$\begin{aligned} kt_i + \log_e (v_i' - v_i) &= \log_e \{(v_\infty - v_0)(1 - e^{-k\tau})\} \\ &= \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.4) \end{aligned}$$

Hence we have only to plot $\log_{10}(v_i' - v)$ against t; the straight line so obtained will have a gradient $-k \log_{10} e$.

It is to be especially noted that in this treatment every actually observed reading is used once and once only and there is no extrapolation. The longer the constant interval τ the greater the value of $v' - v$ for a given t and the more accurate the method. Provided τ is several times as great as the time of half completion of the reaction, the accuracy will be of the same order as in taking n ordinary readings and further taking n readings of the end-point spread over an interval of time equal to that spent on the ordinary readings; in fact it is equivalent to obtaining a very accurate end-point and using it in the usual manner.

This method has been used for some time in this laboratory. Its value may be gauged from the two tables which give the results from an actual experiment. The individual readings are correct to ·01. The observed end-point was 6·49 ± ·01; the value obtained by simple extrapolation is the same, and it is doubtful if any more elaborate method could fix it more exactly without first determining k. In Table I. the

data are treated in the usual way using the values 6·48 and 6·50 for the end-point. It will be observed that the values obtained for k differ from each other by 2·3 per cent. In Table II. the same data are treated by the new method using for τ the periods $1\frac{1}{2}$ hours and 2 hours ; the two values obtained for k agree to within 0·3 per cent. The values of k given in the tables were obtained by plotting $\log_{10}(v_\infty - v)$ and $\log_{10}(v' - v)$ against t on a large scale. In every case a good straight line was obtained with no visible trend. As a small scale reproduction of the plots would be of no interest, we give instead, in the columns headed $(v_\infty - v)$ calc. and $(v' - v)$ calc. the values corresponding to the straight lines of our plots.

Incidentally the end-point is probably obtained most accurately by intrapolation between the two assumed end-points using the value for k obtained by the new method. We thus find $v = 6{\cdot}487 \pm {\cdot}002$.

Laboratory of Physical Chemistry,
Polytechnic Institute, Copenhagen.

XLVII. *The Basis of Acoustic Measurements by Reverberation Methods.* *By* A. H. Davis, *D.Sc., Physics Department, The National Physical Laboratory* *.

Abstract

Following a short account of the derivation of the theoretical equations of reverberation, and a resumé of the experimental laws established by W. C. Sabine, the physical phenomena involved in reverberation measurements are discussed. Conclusions are drawn as to the conditions under which measurements may be made.

The measurement of transmission through partitions by reverberation methods is also discussed, both for the case where the transmitted sound is observed just after passing through the partition, and for a modification in which it is studied in a reverberant condition in a large room.

Introduction.

In connexion with the design of chambers for the test, by reverberation methods, of the acoustic properties of materials and of sound sources, a short account is available[1] of the construction of the laboratory designed by Sabine for this purpose. Information concerning the basis of the work

---

* Communicated by the Author.

is, however, somewhat scattered, and the present paper sets out a short critical survey of the theoretical and experimental considerations upon which reverberation tests are based, and the conditions under which measurements may be made.

When a source of sound is started in a room, it gradually fills the room with sound of increasing intensity until the increasing absorption of sound energy by the walls just balances the emission of the source, and a steady state is established. The general intensity of this steady state depends upon the strength of the source and of the absorbing power of the room. Owing to interference phenomena, there is a complicated distribution of maxima and minima of sound throughout the space, and this makes it difficult to assess the average acoustical energy in this steady state. Sabine, however, established that it could be assessed from the duration of audibility of the sound within the room after the source has ceased. Naturally, the sound dies away in "waves" due to shifting of the interference system; but the ear is able to ignore these fluctuations by concentrating upon averages over finite short intervals, and so gives a measure of the duration of audibility largely unaffected by the interference phenomena. The evidence for this will be considered later. Sabine also established that the intensity so assessed depended in a simple manner upon the strength of the source and upon the absorbing power of the room. He was thus led to use the method in measuring on the one hand the absorbing power of material, and on the other the rate at which sound entered through a small test partition into an otherwise soundproof room.

THEORY.

Theories correlating the duration of audibility with the strength of the source and the nature of the room have been given by W. C. Sabine[2], Jaeger[3] and Buckingham[4]. In all cases it is recognized that a sound suffers some two or three hundred reflexions before it finally dies away, and, in consequence, it is assumed that through random arrangement the sound-energy rapidly becomes uniformly distributed throughout the enclosure. Interference phenomena are ignored, and so results are only valid to the extent to which this is justifiable.

Jaeger's analysis may be summarized as follows:—Sound-waves from a simple source of musical sound in an enclosed space proceed outwards and suffer reflexion, diffraction, and absorption at the various enclosing surfaces. If for a ray of sound the mean number of incidences upon the surfaces is n per second, and if the mean absorption-coefficient (or ratio of absorbed to incident energy) of the surfaces is a, and if the mean intensity (energy per unit volume) in the room at a given instant is I, then the change of intensity by absorption at the surfaces in a time dt is $d\mathrm{I} = -\mathrm{I}.a.n.dt$.

By a statistical method it is shown that for a ray of sound in a closed room the mean number of reflexions per second is given by $n = v\mathrm{S}/4\mathrm{V}$, where

V = total volume of room,
S = total surface of room,
v = velocity of sound.

If E denote the rate of emission of energy from the source, the total rate of change in unit volume of the room is given by

$$d\mathrm{I}/dt = \mathrm{E}/\mathrm{V} - va\mathrm{SI}/4\mathrm{V}. \quad . \quad . \quad . \quad . \quad (1)$$

This is the fundamental differential equation in reverberation work.

Buckingham's treatment is slightly different. He assumes that the sound-energy is divided up into a large number of equal parts, and that in the steady state these energy units are uniformly distributed throughout the room both with regard to position and direction of motion*. Each is assumed to move with the velocity of sound. He shows that when the intensity in the room is I (*i. e.* I energy units per unit volume) the number reaching any element of boundary surface $d\mathrm{S}$ in unit time is $\frac{1}{4}\, v.d\mathrm{S.I}$. On incidence a fraction $\frac{1}{4}\alpha.v.d\mathrm{S.I}$ is absorbed or transmitted and the remainder reflected back into the room. By writing $\int_0^{\mathrm{S}} \alpha d\mathrm{S} = a\mathrm{S}$, the differential equation (1) is obtained, as before, to represent the rate of loss of sound from the room.

The following solutions of equation (1) relate to special circumstances stated :—

(1) Uniform sound-emission beginning at zero time :

$$\mathrm{I} = \frac{4\mathrm{E}}{va\mathrm{S}}\left(1 - e^{-va\mathrm{S}t/4\mathrm{V}}\right). \quad . \quad . \quad . \quad . \quad (2)$$

(2) Steady state reached by uniform emission :

$$\mathrm{I}_{\mathrm{max.}} = \frac{4\mathrm{E}}{va\mathrm{S}}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

---

* Before establishing his formula, Buckingham discusses the acoustical condition of the air in a closed room rather fully.

(3) Emission stopped in steady state (Sabine reverberation case).

$$I = I_{\text{max.}} e^{-vaSt/4V} = \frac{4E}{vaS} e^{-vaSt/4V}. \quad . \quad . \quad . \quad (4)$$

Sabine expressed much of his work in terms of the time taken for a sound to die away to the threshold of audibility, and adopted as his standard initial condition an average intensity $I_{\text{max.}}$ equal to one million times the threshold value. In this case

$$10^{-6} = e^{-vaSt/4V},$$

whence, on putting $t = T$ for this standard condition, we have

$$T = \frac{55{\cdot}2V}{vaS}.$$

This becomes

$$T = 0{\cdot}05V/aS \text{ in feet units}, \quad . \quad . \quad (5)$$

$$T = 0{\cdot}162V/aS \text{ in metre units}. \quad . \quad (6)$$

In effect, Sabine's own theoretical treatment established (4) in the form $I = (E/VA)e^{-At}$. He also calculated that A is related to the mean free path of sound in a room by the equation $p = aV/A$. If we recognize that p has the statistical value $4V/S$ calculated by Jaeger, Sabine's equation becomes identical with (4).

SABINE'S EXPERIMENTAL WORK.

After attempts to study the decay of sound in a room by instrumental means, W. C. Sabine[5] finally decided to measure instead the duration of audibility as perceived by the ear. In an ordinary lecture-room, irregularities in observed duration of audibility were made surprisingly small by working at night. To secure accuracy it was necessary to suspend operations on the approach of a street car within two blocks, or the passage of a train a mile distant. Concerning the accuracy of observations, Sabine states that for a certain case individual values differed from the mean of twenty observations by not more than 0·31 second in any case, and by 0·11 second on the average. The computed "probable error" of a mean of 20 observations was 0·02 second: in ten means the maximum deviation from their average value was 0·05 second. Values obtained were satisfactorily reproducible. Indeed, observations taken every few nights for two months in the Fogg Museum Lecture Room gave values varying from 5·45 to 5·62 seconds, with a mean of 5·57 seconds, a result which was again obtained after the lapse of one, and then of three years.

EXPERIMENTAL LAWS OF REVERBERATION.

Sabine conducted a number of experiments to determine the laws of reverberation. His description of the work is historical in form, and the earlier results are not corrected for variations in the initial intensity of the sound. However, Sabine later recognizes the need for the correction, and then refers back to the earlier work.

Sabine found experimentally :—

(1) The duration of audibility of the residual sound was nearly the same in all parts of the auditorium (Steinert Hall, Boston).

(He found 2·12, 2·17, 2·23, 2·20, 2·23, 2·27, 2·20, 2·26 seconds in various parts of the hall. There was no systematic evidence of increasing audibility at greater distances from the source. The variations are within the limits of accuracy of the experiment. Numerous later experiments, carried out more accurately but with other objects in view, have confirmed the above result.)

(2) The duration of audibility was nearly independent of the position of the source.

(3) The efficiency of an absorbent was, under ordinary circumstances, nearly independent of its position.

(4) In a number of rooms the relation between reverberation T and introduced absorbent X was hyperbolic in form, such that $(X+C)T=k$, where k was a constant for a given initial intensity, and the constant C presumably represented the initial absorbing power (aS) of the room.

(5) The absorbing powers of various arrangements of certain cushions were proportional to the areas exposed. The absorbing power of an open window was proportional to the aperture area.

(6) The constant k was proportional to the volume of the room (range studied—65 cu.m. to 9300 cu.m.). When reduced to standard initial intensity the value of k is given by

$$k=0{\cdot}164V, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

whence in open-window units,

$$T=\frac{0{\cdot}164V}{aS}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

(7) As expected, the decay of sound in a room was exponential in form. It was related to the absorbing power aS of the room—as determined in open-window units from the hyperbolic law—in a manner which agreed with theoretical considerations.

This work on the rate of decay of sound is described in greater detail below.

THE RATE OF DECAY OF SOUND IN A ROOM.

In the study of the rate of decay of sound in the room, Sabine employed his "multiple organ-pipe" experiment. Note was made of the duration t_1 of audibility in a room when a certain source was used, and of the duration t_n when a combination of sources having n times the activity was employed. It follows from (4) that a relation should be obtained of the form

$$\log n = A(t_n - t_1), \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where A, defined by Sabine as the rate of decay of sound in the room, has the value $vaS/4V$ according to Jaeger's theory.

Sabine first verified experimentally that such a logarithmic relation was satisfactory, and from his results he determined A.

The actual experiments were carried out first with one organ-pipe, and then with 4 (or 16) similar pipes, each with its own wind-chest, sounded simultaneously. Provided there was no mutual action between the pipes, the emission in the latter case was four times that in the former.

As regards the technique of the experiment, one, two, three, and four pipes were used. The two- and three-pipe tests were made with various combinations, and so presumably eliminated any interference arising from the position of a given pipe.

Sabine also states that in a certain experiment he used four organ-pipes at a minimum distance apart of 5 metres, because, if placed near each other, four pipes sounded together do not emit four times the sound emitted by one. Such separation is stated to be particularly necessary for large pipes and low tones: much less separation would suffice for the higher tones.

Having determined A, Sabine then investigated its relation to the absorbing power of the room as obtained in open-window units from the hyperbolic law. On the assumption that the absorption of sound in a room takes place on reflexion at the various surfaces, Sabine expected a relation of the form $A = (v/pS)aS$, where p is the mean free path in the room. From a variant of this equation Sabine determined the value of p for two rooms, and found them to be reasonable and to be proportional to the linear dimensions of the rooms.

With further reference to the absorbing power of a room, Sabine states that practically no damping arises from viscosity of the air. He quotes experiments conducted in two very similar rooms, bare and unfurnished, with walls of very small absorbing power and differing 35 fold in size. The absorbing power was found to be accurately proportional to areas. He states if the air-damping were even one fiftieth of the surface damping, the effect wonld have been noticeable.

DISCUSSION OF THE LAWS OF REVERBERATION.

Sabine's experimental propositions lead to the following deductions:—

(1) Since the duration of audibility is practically the same in all parts of the auditorium, we may infer that reverberant sound is uniformly distributed throughout the space, and that the threshold sensitivity of the ear is sensibly independent of whether it was initially subjected to the loudness of an antinode or of a node. Presumably, however, fatigue of the ear would become important with extremely rapid decay of sound.

(2) Since the duration of audibility was nearly independent of the position of the source, we may infer uniform mixing of the reverberant sound, and also that the same amount of energy was emitted by the source in the various positions. This is important because the proximity of objects and walls can affect the output from a source to some extent by tending to put the air near the source in phase or out of phase with the issuing disturbance. Indeed, Sabine[6] quotes a case where the output of a source was considerably affected by alteration of the interference system in the room.

Reaction upon the source would be specially pronounced when the frequency concerned is near one of the resonant frequencies of the air of the room or of one of the walls etc. The author observed a case in which the pitch of a note emitted by a loudspeaker was ultimately sharpened by about 0·05 per cent., and thus brought into unison with a natural frequency of the room: the struggle lasted several seconds. While it may not be absolutely necessary to avoid frequencies of resonance in reverberation work, it appears desirable to do so. Regions of marked resonance are always narrow in the frequency range.

(3) Since the efficiency of an absorbent was, under ordinary circumstances, nearly independent of its position, we may infer uniformity of mixing of the sound, equal incidence upon all parts of the boundary of the room, and that the output from the source was not affected by change in the interference pattern of the room resulting from the introduction of the material.

(4) That the relation between duration of reverberation and introduced absorbent was hyperbolic in form agrees with equations (5) and (6), which were based upon assumptions of uniform mixing of sound, both as regards position and direction, of constancy of absorbing power for various intensities of incident sound, and of constant emission from the source.

(5) That the absorbing powers of various arrangements of material or of open window were proportional to the areas exposed has the same implications as (4). It is well, however, to face the difficulty that—on the ordinary hydrodynamical theory of sound—when an aperture is small compared with the wave-length of the sound concerned, it does not transmit the same amount of energy as that crossing an equal area in the primary waves.

For a circular aperture about 82 per cent. is transmitted, but for a long narrow slit whose breadth is small compared with the wave-length the energy transmitted may even considerably exceed that corresponding to an equal area of wave-front in the primary waves. It is important, therefore, for correct absolute results that areas be not small compared with the wave-length. Indeed, P. E. Sabine[7], working more recently than W. C. Sabine under the improved conditions afforded by the Wallace Clement Sabine Laboratory, has found that when the dimensions of a highly absorbent sample are not great compared with the wave-length of the sound, then the apparent absorbing power per unit area is a function of the area of the sample, of its shape, and also of its location relative to other absorbing surfaces. Measurements were made with areas ranging from 0·14 to 10·0 square metres. For felt, at the frequency for which its absorption is a maximum, namely 1024 d.v., the absorbing power per unit area decreased with increasing area, the ratio in extreme cases being about 3 to 1. At other frequencies the variations were not so great. Long narrow shapes with an area of 3·3 square metres showed an absorbing power some 50 per cent. greater than an equal area in the form of a square.

P. E. Sabine also measured the passage of sound through rectangular openings, similar in shape, but varying in size from 0·34 to 2·8 square metres. The effect observed was the same as in the case of absorption by felt. For example, the relative transmissions of C_4 (512) per unit area through the smallest and the largest openings were in the ratio 11 : 8.

The results obviously suggest some qualifications in the definition of sound-absorption coefficients. Even if a number of materials of equal small area were compared, true relative values of absorption-coefficients would not be obtained: there would be a correction factor depending upon the coefficient observed and due to the difference between the absorbing power of the material and the absorbing power of the wall in the neighbourhood of the sample.

Another point also arises here. If very large samples are used, it may well prove that with very absorbent materials the assumed uniformity of mixing of reverberant sound throughout the room may be affected, unless the total area of the surfaces of the room is large compared with the area of the sample. The need for very large rooms is thus clear. Information as to the minimum size necessary is not available.

(6) That the constant k is proportional to the volume of the room agrees with the theory indicated. The correspondence between Sabine's experimental result $k/V = 0{\cdot}164$ and the theoretical value 0·162 deducible from equation (6) is most striking. It implies—if everything else is satisfactory—that Sabine's open-window standard had an absorption-coefficient which was almost exactly unity on the absolute scale. Indeed, it is probable that if this had not been the case, Sabine would have found absorbing power not to be proportional to window aperture.

(7) That the decay of sound was logarithmic in form agrees with equation (4). This equation assumes the absorbing power of the room to be independent of the intensity of sound within it. Departure from the law would be expected if the ear were seriously affected by the interference phenomena, or if the threshold sensitivity of the ear depended markedly upon the initial intensity in the room. Sabine's experiments have been repeated over a vastly wider range with loudspeaker apparatus which avoids using simultaneously a number of different sources which may

react upon one another. No departure from the logarithmic law has been observed.

By conducting experiments with two different initial intensities of sound of known ratio, the actual sensitivity of the observer's ear is eliminated.

Summarizing the points raised, it appears that in reverberation measurements of absorbing power the dimensions of the sample should be large compared with the wavelength of sound, and small compared with the dimensions of the room. Large rooms are thus indicated. To average out any lack of uniformity of distribution of sound within the room, the positions of source, material, and observer should be varied: satisfactory rooms should show little dependence upon position. Particularly for frequencies near resonant frequencies of the air of the room or of any of the walls, reaction upon the source may affect its output: the proximity of other sources emitting at the same time may also affect output. It is thus desirable, to avoid resonant frequencies, to use a single source, and in each position to vary its output in a known manner. The source should be of a type which is affected as little as possible by reaction effects. Large rotating reflectors in the room would tend to average out errors due to lack of uniformity of sound within the room, due to reaction upon the source, or due to any effect the interference fluctuations may have on the ear during the decay of sound. By conducting all experiments with at least two different intensities of initial sound—of known ratio—the characteristics of the ear are largely eliminated.

APPLICATION OF REVERBERATION METHODS TO TRANSMISSION MEASUREMENTS.

W. C. Sabine[8] also applied a reverberation method to measuring the transmission of sound through partitions. Before discussing the method, we may note that transmission of sound through partitions may take place by a variety of agencies. The sound may pass through cracks or pores in the panel, it may be transmitted by true sound-waves set up in the material of the panel by incident aerial sounds, or by the panel vibrating as a whole like a diaphragm and thus communicating the vibrations to the air on the other side. For solid panels the true acoustical transmission must usually be negligible owing to the great difference in density between the air and the panel, and the main transmission is by means of vibrations as a whole.

A vibrating panel will have certain natural frequencies at which it will respond and transmit sound more freely. In any transmission tests it is thus desirable to use pure tones, and to cover a range of pitch. The resonant frequency will depend upon the size of the panel and upon its method of fixing, so that, while information concerning transmission at resonance for particular panels may be of value, figures obtained away from resonance regions will be of more general application.

In W. C. Sabine's reverberation method of measuring transmission, the partitions were built into an aperture in the double wall between two adjacent but structurally separate rooms. Broadly the method consisted in producing, by means of a source in the larger room, a volume of sound of which the intensity in terms of threshold audibility was known, and then, by stopping the source, allowing the sound to decay at the rate natural to the room until it ceased to be audible on the other side of the partition. The intensity of the sound at this instant was estimated from reverberation measurements in the source room, and was taken to be numerically equal to the coefficient of transmission of the partition. In later work carried out in the specially designed Wallace Clement Sabine Laboratory of Acoustics, P. E. Sabine determined simultaneously the duration, after the source had ceased, of the residual sound in the source chamber and in the adjacent test chamber, and computed from these results the ratio of intensity on the two sides of the partition.

It is clear that, to obtain a simple transmission-coefficient directly from such experiments, the receiving-chamber must have absorbent walls in order to ensure that the entering sound is heard alone, without any enhancement arising from reflexions and reverberation. The listener in this case should be situated close to the panel, for there the entrant sound has not been enfeebled by spreading. P. E. Sabine [9] observed experimentally that the acoustic condition of the room does affect the values of apparent transmission, and that the effect was least pronounced when observations were confined to positions near the transmitting panel. He adopted this position as his normal procedure.

In such tests the duration of audibility is not heard under precisely the same conditions in the two rooms. In the source-room the sound-energy is moving to and fro in all directions; in the receiving-room it has a general inward direction. It seems unlikely that the ear would differentiate, but experiment alone can decide this.

The author[10] recently derived equations for the decay of the reverberant sound in each of two adjacent rooms as used for transmission tests, when the receiving-room is not completely absorbent. These indicate how the reverberant sound in the second room depends upon its acoustic condition, and that the reverberant sound may be appreciable in comparison with the undiffused entrant sound.

The equations, however, also suggest an alternative method of measuring transmission: namely, by making both rooms reverberant and listening in the receiving-room to the diffused reverberant sound rather than to the sound near the panel which is just entering the room. While the general equations are complicated, they are greatly simplified if the transmittance through the panel be small, and become very simple if the source-room be sufficiently more reverberant than the receiving-chamber.

Simultaneously Buckingham[11] published equations for the case of low transmittance, which correspond exactly with a special case of the equations referred to above. While he expresses a preference for equal rooms—which also give simple relations,—he recommends for accuracy that, if the two chambers are not equally reverberant, one should be markedly less reverberant than the other.

Buckingham suggests, however, that the more reverberant one should be used as the receiving-chamber, on the ground that for a given activity of source the duration of audibility in it will otherwise be too short for accurate observation. However, there is a somewhat remarkable reciprocal property of symmetrical partitions, deducible from even the most general relations, that the reverberant sound in a room A due to a source in a room B is identical with that in the room B due to a source of the same activity in A. The argument, on the basis of longer audibility, to use the larger room as the receiving-room is thus untenable. On the other hand, as regards duration of audibility in the source-room, it is found to be best to have the source-room the more reverberant—the case studied in my earlier paper.

This latter arrangement of markedly different rooms also gives simpler equations in that the rates of decay in the two rooms are the same, whereas if the receiving-room be the more reverberant, the two rates of decay would be different and the experimental procedure would probably be more involved.

In some conditions, however, equations given for reverberant sound in the receiving-room may not represent the sound actually heard at special points (such as near the panel), owing to the sound which is proceeding direct from the panel and which has not yet been generally diffused by reflexion. When the source-room is the more reverberant, the entrant sound can be made to die away at the same rate as the reverberant sound—a possible simplification. If, however, the receiving-room be the more reverberant, the entrant sound would die away at a greater rate than the reverberant sound, and undoubtedly it could be arranged to decay so rapidly that an ear in the receiving-chamber would ultimately be listening only to the decay of sound which had been well diffused by repeated reflexions, and which obeyed the reverberation equations.

If this early suppression of the entrant sound be vital for reverberation work—one can hardly say without experiments,—the advantages associated with a more reverberant source-room or with equally reverberant rooms would have to be sacrificed.

Apart from these special points in transmission measurements, the general conditions necessary for reverberation work need to be fulfilled. Large rotating reflectors in the source-room are especially necessary in order that, in spite of interference phenomena, the average intensity of sound against the partition in a series of observations should be equal to the average in the room. It was apparently for this reason that W. C. Sabine introduced rotating reflectors. He also enclosed the observer's seat in a box, so that the condition of the room was rendered independent of the presence or absence of the observer. Any resonance frequency of the connected rooms should be avoided, for the information obtained might express the peculiarity of the laboratory rather than a property of the panel.

As Buckingham points out, in the source-room the absorptivity of a feebly-transmitting partition will not usually be very different from that of the remainder of the walls, and the presence of the panel will not cause any serious departure from the uniformity of energy distribution assumed in the theory. However, in the receiving-room the panel alone is acting as source, and the uniformity of distribution will be improved if the area of the walls of this room be large in comparison with the area of the panel.

For panels of high transmittance, however, the area which is a source of sound for one room is a sink of sound for the other, and both rooms must be large.

Summarizing the position with respect to transmission measurements, conditions in the source-room must generally satisfy the requirements set out previously in connexion with absorption measurements. In particular, rotating reflectors or some equivalent appear desirable. If highly-transmissive—or very absorbent—panels are tested, the source-room will need to be large in comparison with the area of the test partition, but for ordinary hard and moderately sound-proof partitions this requirement is less pronounced.

If the receiving-room is used after the manner described by Sabine, it should have absorbent walls and be non-reverberant. It may be small.

If the receiving-room is reverberant and attention is directed to the reverberant sound within, the room must be large in comparison with the area of the test panel. Simplest relations are obtained if it is less reverberant than the source-room; but to ensure early suppression of the sound entering the receiving-room, it may be necessary to make the receiving room the more reverberant.

February 1926.

References.

1. P. E. Sabine, 'American Architect,' cxvi. (July 30, 1919).
2. W. C. Sabine, 'American Architect,' lxviii. (1900); 'Collected Papers,' p. 43, 1922 (Harvard Univ. Press).
3. G. Jaeger, *Akad. Wiss. Wien. Sitz. Ber.* cxx. 2*a*, p. 613 (1911).
4. E. Buckingham, Bur. Stds. Sci. Papers, No. 506, 1925.
5. W. C. Sabine, *loc. cit.*
6. W. C. Sabine, 'Collected Papers,' p. 278.
7. P. E. Sabine, Phys. Rev. xix. p. 402 (1922).
8. W. C. Sabine, 'Brickbuilder,' xxiv. p. 31 (1915); 'Collected Papers,' p. 237.
9. P. E. Sabine, 'American Architect,' July 28, 1920.
10. A. H. Davis, Phil. Mag. l. p. 75 (1925).
11. E. Buckingham, *loc. cit.*

XLVIII. *On the Effect of the Shape of the Cathode on the Glow Discharge.* *By* W. Stephenson, *M.Sc., Armstrong College, Newcastle-on-Tyne* *.

Introduction.

THE effect of the shape of the cathode on the current, Crookes's Dark Space (C.D.S.) thickness, and cathode fall of potential of the glow discharge, has received attention by Aston † and others, and recently by Gunther-Schulze ‡ and Prof. M. E. Hufford [*]. Gunther-Schulze experimented upon a current-increasing effect that occurs under certain circumstances between equipotential cathode surfaces; Hufford upon phenomena at a hole in a cathode, and discharge between equipotential cathodes. The object of this paper is to describe a current-increasing and cathode fall of potential decreasing effect, thereby serving as an introduction to the general effect touched upon in various aspects by the above workers.

---

* Communicated by Prof. Geo. W. Todd, M.A., D.Sc.

† F. W. Aston, Proc. Roy. Soc. A. lxxxvii. p. 428 (1912).

‡ A. Gunther-Schulze, *Zeit. für Physik*, xix. p. 313 (1923).

General features of the work can best be stated here. The glow discharges are free from positive column, so that the voltage across the discharge-tube terminals is nearly the same as the fall of potential between the cathode and the boundary of the C.D.S. and the negative glow. The glass vessels containing the electrodes were large compared with the size of the electrodes; and air, dried by phosphorus pentoxide, was the gas through which the discharge was passed. The voltage supply was the 480 d.c. city mains, dry batteries, and an "Anode Converter" which provided about 500 volts.

I. EXPERIMENTS WITH COMPOUND CATHODES.

Some striking phenomena occur when the usual simple cathode is replaced by a variety of slightly complex cathodes, and with compound cathodes, two disturbances of the uniformity of the glow discharge are illustrated :—

(i.) A current-increasing effect, evinced by an increased brightness of the negative glow, measurements of current density, and reduction in the thickness of the C.D.S.

(ii.) A reduction in the cathode fall of potential, evinced in part by a decrease in the total voltage across the discharge-tube terminals, and in part by the appearance of the negative glow under "normal" conditions (when the voltage across the discharge tube remains constant at a minimum value, and the current denity is maintained at a constant value by self-adjustment of the available cathode area utilized in the discharge).

Two Parallel Wires as Cathode.

A discharge tube was constructed in which three co-planar parallel aluminium wires A, B, and C, each 5 cm. long, 1 cm. apart, were used as electrodes. A was used as anode, and B and C together served as cathode. At pressures in air of the order 1 mm. Hg, in the "abnormal" current conditions both B and C are surrounded by a uniform cylindrical negative glow, the radial C.D.S. thickness being the same for B as for C. The equations

---

[*] M. E. Hufford, Phil. Mag. vol. l. p. 1197 (1925).

$$p.d_n = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{I_n}{p^2} = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

give the approximate relations between the "normal" C.D.S. thickness (d_n), the "normal" current density (I_n), and the pressure (p).

At lower pressures, when the "normal" thickness of the C.D.S. for a particular pressure becomes greater than half the distance between the wires B and C, the uniformity of the negative glow is destroyed, and the space immediately between B and C shows a brighter glow, and a smaller C.D S. thickness, and therefore a greater current density, than the space to the left and right of the two wires. This superior brightness persists under the "normal" discharge conditions. At a lower pressure, the bright parts become separated, and discharge does not pass in the straight line joining B and C. In this case the negative glow for the "normal" condition consists of only the bright part of the glow, lying between, but above and below, B and C. This suggests that the "normal" cathode fall of potential for the bright part of the glow is less than that for the glow to the left and right of B and C under the same pressure conditions.

A Spherical Spiral Cathode.

A further degree of the same effect is shown in the glow discharge of a point anode at the centre of a spirally wound spherical cathode. An anode wire, 1 mm. diameter, was covered with glass tube to within 3 mm. of its end and was placed at the centre of a sphere, made in spiral form from the same wire.

The usual discharge characteristics were obtained at pressures of the order 1 mm. Hg, and equations (1) and (2) obtain. At low pressures the effect occurs that is described above for the cathode of two parallel wires; and at a pressure depending upon the distance apart of the adjacent rings that constitute the spiral sphere, the "normal" negative glow consists of only a continuous bright spiral lying between the adjacent wires of the spiral. At still lower pressures, when the C.D.S. thickness becomes of the order of the distance between the adjacent rings, there are two distinct parts of the negative glow:—an inner sphere of negative glow, concentric with the cathode, and brighter than the other, and an outer sphere of negative glow. At pressure 0·05 mm. Hg, the outer C.D.S. may have a thickness of 2 cm., while at the same time the inner C.D.S. is only 0·5 cm. thick. Under such circumstances the "normal" discharge condition is characterized by complete absence of the onter negative glow, and only the inner face of the sphere is utilized in the discharge. There are thus two effective conditions at this cathode :—

(A) The current-increasing effect of the concave cathode surface of the sphere.

(B) A current-increasing effect of the same nature as that described in the case of the two parallel wires.

Both are accompanied by a decrease in the cathode fall of potential.

Of particular interest is a bright "bead" of glow that was situated in the centre of the first spiral of one of the spherical spiral cathodes that was used. The first spiral left, as it were, a hole in the cathode surface that was wider than the distance between the adjacent rings of the cathode. At these low pressures this cathode acted in the same way as did the cathodes used by Hufford *. The bright "bead" increased in length, and decreased in thickness, for decrease in the total currrent through the discharge tube; it was, under all conditions of current, brighter than any other part of the negative glow, and was brighter the greater the current through the tube. These characteristics suggest that the "bead" is of the nature of the usual negative glow, resulting as a combination of the two current-increasing conditions (A) and (B) ; but the round bead-like end was always turned away from the anode, and under certain conditions its colour suggests that it is of the nature of a positive column striation.

Concentric Cylindrical Spirals as Cathode.

The two effects (A) and (B) are shown in a cathode consisting of two concentric cylindrical spirals that are used together as cathode, the anode being a straight wire passing down the axis of the cylinders. Such a discharge tube was made of 2 mm. diameter iron wire, the cylinders being 4·5 and 2·5 cm. diameter respectively.

Using the inner cylinder alone as cathode and the central wire as anode, the phenomenon occurs that is indicated above for the spherical cathode. When both cylinders are used together as cathode the effect of the opposing cathode surfaces (B) is greater, at a suitable pressure and current, than the effect (A) due to the curvature of the cathode. After passing through the stages corresponding to those for high pressures for the spherical cathode, the condition is reached at which the "abnormal" currents are represented by three negative glows. First, there is a cylindrical negative glow surrounding and co-axial with the outer cylindrical spiral; secondly, a much brighter negative glow in the annular space between the two cylinders; thirdly, a negative glow that is not so bright as the second, but brighter than the first, situated in the inside of, and co-axial with the inner cylinder. Under pressure conditions that depend upon the dimensions of the cylinders, the annular negative glow is easily the brightest of the three, and in such a case, as the current through the tube is reduced, the outermost glow disappears first, then the innermost follows, and the "normal" condition is represented by only the annular negative glow. Since the curvature is greater for the inner cylinder than for the outer one, the current-increasing effect due to curvature should be less for the annular space than for the innermost space between the anode and the inner cylinder. In the above case the current density is greater in the annular space than in the space between the anode and the inner cylinder. Thus the very bright annular glow indicates a current-increasing and cathode fall of potential decreasing effect due to the opposing surfaces offered by the inside of the outer and the outside of the inner cylinder. The effect due to a concave cylindrical cathode surface is a particular case of the general effect due to two opposing cathode surfaces.

---

* *Loc. cit.* p. 1197.

At the time of writing this paper, Hermann Schüler* gives, in the January 9th number of the *Zeit. für Physik*, some interesting results and uses of the inner glow to a cylindrical cathode.

II. The Discharge between Equipotential Plates.

The U-shaped Cathode.

Quantitative work is possible with discharge tubes of the above types, but a U-shaped cathode and electrode disposition of the kind used first by Gunther-Schulze simplifies description and facilitates measurement of, and more clearly exemplifies, the current-increasing effect, while at the same time making possible a ready comparison between current conditions to a plane cathode and a cathode consisting of two equipotential parallel plates. For a detailed account of the discharge to a U-shaped cathode one is referred to the work by Gunther-Schulze * on the effect of the shape of the cathode on the current of the glow discharge in hydrogen. The following experiments illustrate the work that is possible with a U-shaped cathode in air.

---

* Hermann Schüler, *Zeit. für Physik*, xxxv. p. 323 (Jan. 1926).

Two exactly similar strips of brass, approximately $6{\cdot}0 \times 0{\cdot}85 \times 0{\cdot}1$ cm., were used as electrodes, one (k) being bent to a U-shape, with arms 0·5 cm. apart, and the other (I) used flat. One could be used as anode and the other as cathode. With the I-electrode as cathode, the value I_n of the current through the discharge tube when the cathode is just completely covered with the negative glow (or the value when the voltage across the discharge tube terminals begins to remain at a constant "normal" value, assuming that the current is being reduced from "abnormal" to "normal" values) will give the value I_n/A for the "normal" current density, where A is the area of the cathode surface. Thus I_n at all pressures will give relative values of the "normal current densities for those pressures, and if the same condition holds for the U-electrode it follows that $k_n/I_n = 1$, at each value of the pressure, assuming that the U-electrode is without effect on the current density.

At pressures greater than 0·15 cm. Hg, the values of I_n and k_n are almost identical at a particular pressure. This equality is what is expected, since the negative glows in each case are exactly similar. For very much greater pressures, when the negative glow closely wraps the cathode, the current k_n becomes less than I_n at the same pressure. The current to the inside of the U-shape encounters a higher resistance in the narrow slit of the U than it does for the I-electrode.

The graph, fig. 1, shows experimental results obtained for I_n and k_n over the pressure range 0·16 to 0·02 cm. Hg. Fig. 2 gives the ratio k_n/I_n for a similar set of readings. It is seen that k_n is always greater than the corresponding value of I_n. The negative glow for the U-electrode as cathode is now as shown in fig. 3, a sketch of the glows at

---

* Gunther-Schulze, *loc. cit.*

$p=0{\cdot}06$ cm. Hg, the current being "abnormal." There are two parts of the negative glow :—

Fig. 1.

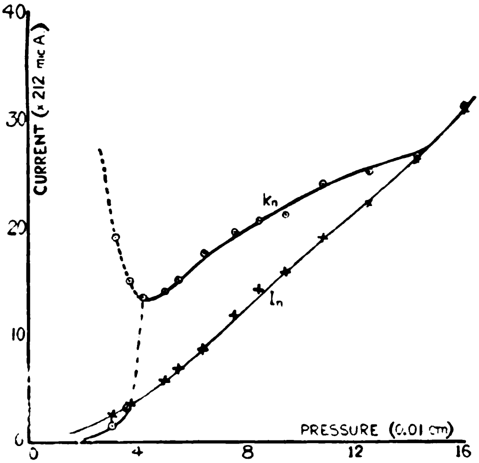
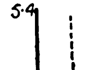


Fig. 2.

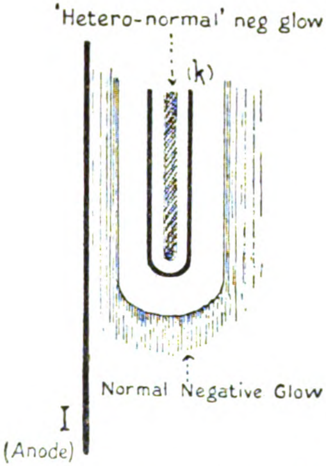


(1) An outer glow, with C.D.S. thickness the same as is obtained for the I-electrode as cathode, at the same pressure and current density conditions.

(2) An inner negative glow, more brilliant and clearly

defined than the outer one, and with a smaller C.D.S. thickness: the current density to the inside is therefore greater than that to the outside at the same pressure. The "normal" condition is represented by complete absence of the outer glow, and the various "normal" currents are accommodated by only part of the opposite faces of the inside of the U being utilized in discharge. As is shown in fig. 1, the "normal" current density to the inside of the U is much greater than the "normal" value that is expected from equation (2). At the same time the voltage across the discharge tube is less than the "normal" value for the particular pressure, for discharge to the I-electrode as cathode. The increase in k_n begins as soon as the "normal" C.D.S. thickness for the outside of the U becomes greater than about half the distance between the opposite arms of the U, as is shown in Table I.

Fig. 3.



At pressures less than 0·02 cm. Hg, k_n is generally less than I_n at the same pressure. The C.D.S. thickness for these pressures is too great to allow entry of the discharge to the inside of the U, and only the outside is utilized in the discharge.

From the experiments it appears that the ratio k_n/I_n reaches a maximum near the pressure 0·03 cm., and then rapidly decreases until, at $p=0·02$, the ratio is less than 1. The decreasing values of the current, however, are obtained under different temperature conditions, and for this reason it is difficult to determine the course of the curve near the pressure 0·03 cm. Hg. At such pressures the current could be one of two values, under the same external circuit and pressure conditions. At $p=0{\cdot}032$ cm. Hg, k_n was 425 or 3028 micro-amperes. The second value existed until the inner space became so hot that discharge between the opposing arms of the U was impossible, and the current dropped to the low value. At the large current densities the voltage across the tube increased, as is shown in Table I., but the voltages were still very much less (100 volts or so) than those obtaining for the low current condition.

TABLE I.

Pressure. cms. Hg.	C.D.S. thickness for inside the U.	C.D.S. thickness for outside the U.	k_n.	$\frac{\mathrm{I}_n.}{2}$	Current to inside of the U. $(k_n-\mathrm{I}_n/2)$	Voltage across terminals.
0·124	0·22 cm.	0·22 cm.	24·8	10·6	14·2	316
0·11	0·23	0·26	23·8	9·7	14·2	311
0·096	0·22	0·29	22·8	8·6	14·2	318
0·085	0·22	0·33	21·4	7·8	13·8	321
0·074	0·22	0·34	19·8	6·2	13·6	326
0·065	0·22	0·39	18·0	5·1	12·9	328
·057	0·22	0·43	16·0	3·9	12·1	345
0·049	0·22	0·46	—	—	—	—
0·043	0·22	0·48	12·6	1·9	10·7	385
0·034	0·22	0·52	—	—	—	—
0·031	0·22	0·55	20·0	1·0	19·0	405

Distance between arms of U-shape 0·5 cm.

A summary will now be useful :—

(i.) Coincident with the very near approach of the boundaries of the C.D.S.'s of two equipotential cathode surfaces that are opposing each other, there occurs a current-increasing effect.

(ii.) The resulting large currents pass at a cathode fall of potential not greater than the cathode fall for the "normal" condition for the same pressure and cathode material, but for the discharge between a plane cathode and anode.

In other words, we have an "abnormal" current passing at the usual, or less than the usual, "normal" cathode fall of potential (whilst, generally, any increase in current above the "normal" results in an increase in voltage, according to an equation of the type given by Aston *). These currents, and voltages, I propose to name "hetero-normal."

(iii.) The voltage increase noted in Table I. shows that the "hetero-normal" effect exists equally well as an "hetero-abnormal" effect. The following experiments will show this more clearly.

III. THE "HETERO-NORMAL" EFFECT.

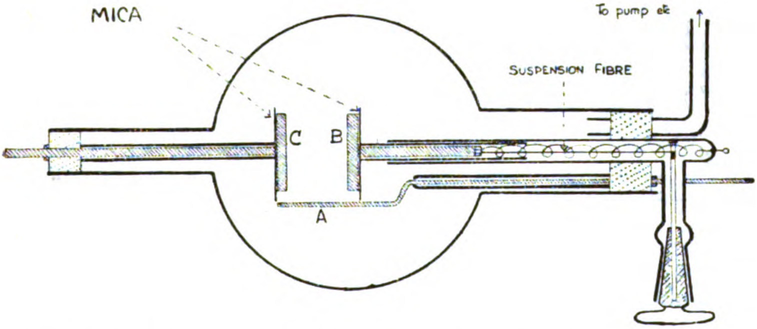
For further experimentation on the "hetero-normal" effect, a discharge tube should provide :—

(i.) means for variation of the distance between the opposing cathode surfaces ;

(ii.) simplification of the discharge conditions, by getting rid of extraneous discharges such as that passing to the outside of the U-electrode.

A simple discharge tube that satisfies these requirements is shown in fig. 4. B and C are brass cathodes, the backs of which are covered with thin mica. Each is 3·29 cm. diameter: leads-in are covered with glass tube, so that discharge is confined to the opposing faces of B and C ; and a glass tap, with central spindle around which a supporting thread runs, affords the means for variation of the height of B above C. B was restricted to vertical movement by a sliding arrangement between two co-axial glass rods (so that the surfaces of B and C were always parallel to each other) as is indicated in the diagram. The anode was a brass rod 5 cm. long, introduced as shown. The electrodes were contained in a 2-litre flask, thus ensuring freedom from "wall" effects. Apart from "hetero-normal" measurements, we have to

Fig. 4.



---

* Aston, Proc. Roy. Soc. A, lxxix. p. 84 (1907).

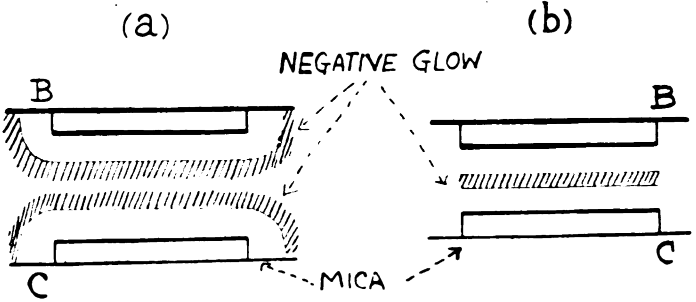
show that the current-increasing, and cathode fall of potential decreasing effect, occurs in the "hetero-abnormal" glow discharge condition.

Variation of the "Hetero-normal" Effect with Change of Distance between the opposing Cathode Surfaces.

The "hetero-normal" effect is obtained in these experiments by varying the distance between the cathode surfaces B and C (now called distance D), and maintaining the current at a value sufficient to just completely utilize the available cathode area in the glow discharge.

An important characteristic of the "hetero-normal," and "hetero-abnormal" glow discharge is illustrated in the type of negative glow that is obtained for various positions of B above C. Fig. 5 (*a*) shows the "normal" negative glow for a value of D greater than about twice the "normal" thickness of the C.D.S. at the particular pressure; for D less than twice the C.D.S. thickness, the negative glow is as shown in fig. 5 (*b*). We see that the essential difference between the "normal" and the "hetero-normal" glow is that the latter is only obtained at the points of intersection of perpendiculars from both the opposing cathode surfaces. Thus, only the opposing faces of B and C are utilized in the "hetero-normal" or "hetero-abnormal" discharge, while the whole cathode area, the rims as well as the faces of B and C, are utilized in the "normal" or "abnormal" discharge. At any pressure, when D is less than twice the "normal" C.D.S. thickness (d_n), a "normal" discharge cannot take place between B and C. However, for any value of D it is possible for an "abnormal" discharge to pass in the space between B and C, because at some high value of the current density the distance D will be equal to

Fig. 5.



about twice an "abnormal" value (d_a) of the C.D.S. thickness. The factor that will decide whether the discharge is "abnormal" or "hetero-abnormal" is the one of difference in cathode fall of potential, and as this experiment will show, the voltage across the terminals of the discharge tube is always less for the "hetero-normal" or "hetero-abnormal" discharge than for the "abnormal." Thus, an electron or positive ion movement that is always perpendicular to both the opposing cathode surfaces, resulting in a decrease in cathode fall of potential, is the chief characteristic of the "hetero-normal" and "hetero-abnormal" discharge.

Table II. gives representative readings of the current (in this case proportional to the current density, since the cathode area is fully utilized in the discharge in each case), the voltage across the discharge-tube terminals at that current value, and the corresponding thickness of the C.D.S. for various pressures and distances D. The table shows that

TABLE II.—Showing variation of I, V, and *d*, for different values of D, the available cathode area being just completely utilized in the discharge.

Pressure cm. Hg.	D cm.	*d* cm.	I (162 . 10^{-6} amp. units).	V volts.	Remarks.
0·111	2·47	0·29	77	340	"Normal" discharge.
	1·88	0·28	78	340	
	1·31	·25	73	340	
	0·96	·28	72	339	"Hetero-normal" discharge.
	0·78	·25	73	330	" "
	0·60	·22	78	327	
	0·55	·18	100	318	
	0·45	·16	133	317	
	0·40	·15	210	311	
	0·31	·12	345	305	
	0·28	·09	690	310	
	0·24	·07	1060	317	
0·078	3·0	0·34	34	336	"Normal" discharge.
	1·94	·34	34	336	
	1·48	·37	33·5	332	
	1·10	·37	34	330	
	0·94	·34	39·8	330	"Hetero-normal."
	0·66	·29	64	329	
	0·55	·21	120	330	
	0·44	·18	240	361	"Hetero-abnormal."
	0·39	·14	370	368	

TABLE II. (*continued*).

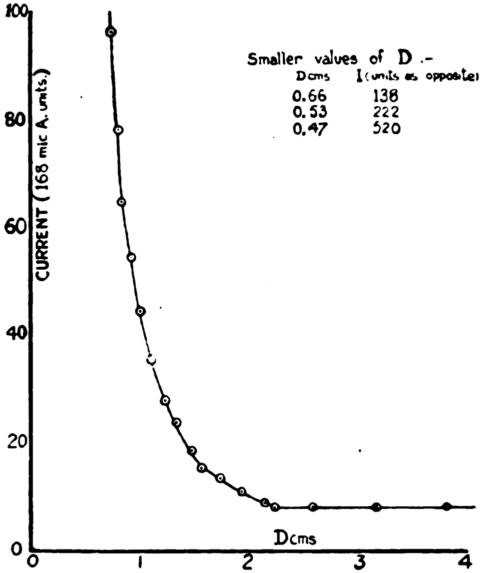
Pressure cm. Hg.	D cm.	*d* cm.	I (163 . 10^{-6} amp. units.)	V volts.	Remarks.
0·057	2·64	0·52	21·5	345	"Normal."
	1·84	·54	21	340	
	1·59	·54	21	340	
	1·34	·49	22	336	
	1·17	·44	26	330	"Hetero-normal."
	1·11	·36	35·5	330	
	0·87	·34	48·5	330	
	0·70	·26	76	330	
	0·58	·20	108	330	
	0·49	·17	190	345	"Hetero-abnormal."
	0·39	·14	385	380	
0·042	3·83	0·83	8·1	385	"Normal."
	3·17	·96	7·8	385	
	2·58	·90	7·8	385	
	2·23	·84	7·8	385	
	2·14	·84	8·6	385	
	1·93	·78	10·8	385	
	1·72	·67	13·0	385	
	1·6	·67	15·1	385	
	1·46	·59	18	373	"Hetero-normal."
	1·32	·51	23·5	370	
	1·22	·48	27·5	364	
	1·10	·42	35	359	
	0·99	·38	44	359	
	0·93	·36	54	355	
	0·83	·33	64·5	353	
	0·80	·30	78	353	
	0·73	·27	96	353	
	0·66	·21	138	346	
	0·53	·19	222	356	
	0·47	·17	520	377	"Hetero-abnormal."

I_n, V_n, and d_n are approximately constant for the larger values of D, but that, as D decreases we have a rapid increase in the current density, together with a decrease in the voltage across the discharge-tube terminals. Graph fig. 6 shows the I–D curve for the results of Table II., at $p=0·042$ cm. Hg. The negative glows corresponding to the current increases are "hetero-normal" so long as the voltage V is less than, or equal to, V_n, the "normal" value of the voltage at that pressure. The higher voltages are generally "hetero-abnormal," due to the fact of heating at the cathode for these large currents, or because there appears to be a minimum distance apart of the surfaces B and C for which a strictly "hetero-normal" discharge can pass, the discharges being "hetero-abnormal" for the distances smaller than this minimum.

The Volt-Ampere Characteristics.

At a particular pressure, D was maintained at various constant values, and the volt-ampere characteristics were taken as a result of varying the current passing through the discharge tube. Table III. shows typical results. For large values of D the discharges were first "normal" and then "abnormal," and the glows are as in fig. 5 (*a*). For the smaller values of D, the negative glow is of the fig. 5 (*b*) type, and the discharge is first "hetero-normal" and subsequently "hetero-abnormal." It is seen very clearly that there is a lowering of the cathode fall of potential in the "hetero-normal" and "hetero-abnormal" discharges. The characteristics at all pressures indicate a minimum cathode fall of potential V_s for a particular value or values of D, the average decrease $(V_n - V_s)$ being 22·5 volts for one series of results over the pressure range 0·1 to 0·04 cm. Hg. At pressures lower than 0·02 cm. Hg, the size of the

Fig. 6.



cathode becomes of the same order as the thickness of the C.D.S. experimented upon, and the symmetry of the glow discharge is disturbed. The empirical equation connecting V and $\frac{1}{\sqrt{I_s}}$ is of the form given by Aston *, except that both the constants E and F are smaller in the "hetero-abnormal" than in the "abnormal" discharge.

TABLE III.—Volt-ampere characteristics for various values of D. Pressure 0·08 cm. Hg.

D cms.	I ($162 . 10^{-6}$ amp. units).	V volts.	*d* cms.	Remarks.
15·0	27	384	·52	Full cathode area utilized. *i. e.* "abnormal" discharge.
	40·5	383	·46	
	53·5	386	·39	
	76	392	·34	
	94	396	·31	
	110	415	·30	
	230	465	·27	
	310	505	·25	
	540	560	·20	No "hetero-normal" effect.
1·14	27·5	390	—	Full cathode area utilized. No "hetero-normal" effect.
	52·5	390	·42	
	76	392	·38	
	118	415	·28	
	140	420	·26	
	260	442	·24	
	360	480	·22	
	600	540	·20	
	620	560	·19	
0·62	32·5	340	·22	Only ¼ area utilized. "Hetero-normal."
	63·5	343	·22	
	94	344	·22	
	117	344	·21	
	152	352	·21	
	190	361	·20	Full area utilized. "Hetero-abnormal."
	320	398	·17	
	475	430	·17	
0·50	31·7	342	·18	"Hetero-normal."
	64	342	·18	
	96	342	·18	
	111	342	·18	
	168	342	·18	
	190	342	·18	
	335	390	·16	Full area utilized. "Hetero-abnormal."
	495	408	·15	
	560	470	·12	

---

* Aston, *loc. cit.*

One matter must be referred to at this stage, because it may be thought that the voltage decreases and the current increases shown in [the above characteristics are due to heating effects.

My introductory work with the compound cathodes has been added partly because the work shows the "hetero-normal" effect under conditions that cannot easily be criticised from the aspect of temperature changes, resulting in the current phenomena. Heat radiation from the cathode surfaces B and C is more difficult the nearer the two surfaces are together; and the surfaces, and the space between them, will heat up more rapidly the nearer they are together. That heating is inadequate to account for the currents can be shown in various ways. Thus at low pressures (corresponding to 0·03 cm. Hg, in the case of the experiments on the U-cathode above), the energy carried up to the cathode for a particular C.D.S. thickness is greater than that carried at a higher pressure (because the cathode fall of potential is greater for the lower pressure), and greater heating is the result. The increased heating results in a decrease in current density, and finally discharge to the space giving the "hetero-normal" effect ceases. If the electrode C is covered with a thin sheet of mica, the heating for B should be present just as for when C was used as cathode. The discharge from B, however, is "abnormal," with essentially the same characteristics as are obtained for larger values of D at the same pressure, and for C covered. If heating the cathode was affecting the discharge in any way we should not expect the clear confinement of the discharge under "hetero-abnormal" conditions to the point of intersection of perpendiculars from opposing cathode surfaces—and this can be tested very conveniently by making the electrode B to be displaced to one side with respect to C. The definite form that Aston's equations* take for the "hetero-abnormal" discharge indicate that heating effects are inappreciable except for very high current densities, a hundred times or so normal. Further, it is likely that heating the gas will result in a decrease in current density in the inner space.

The Thickness of the C.D.S.

The thickness *d*, as well as D, was measured on a vertically travelling microscopic stand, fitted with a sighting tube. The sharp edge of the "hetero-normal" glow made possible accurate measurements of d_s, the "hetero-normal" C.D.S. thickness, even although the maximum value of d_s was only in the neighbourhood of 1 cm. The distance from B to the nearer boundary of the C.D.S. and the negative glow was always the same as the distance C to its nearer glow boundary. Fig. 7 shows typical experimental results. The relation at all pressures is linear, *i. e.*,

---

* *Loc. cit.*

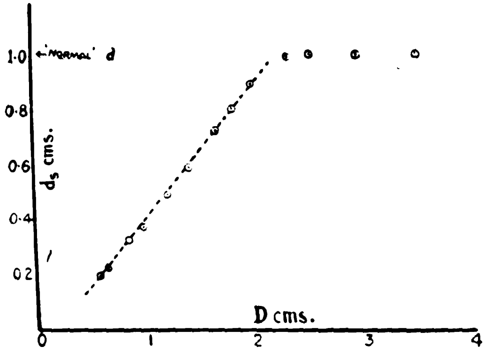
$$d = m\mathrm{D} - r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where m and r are constants. m appears to be the same for all pressures, and r is very nearly zero, the best experimental conditions giving

$$d_s = 0{\cdot}44\ \mathrm{D}.$$

An experiment by Gunther-Schulze* suggested that the decrease in the thickness d_s was inversely proportional to the distance between the opposing cathode surfaces : this is not incompatible with the above equation, because at the small values of D the glows were "hetero-abnormal" and not "hetero-normal."

Fig. 7.



The Variation of d_s with the Current Density.

Aston has shown that two empirical equations connect the magnitudes I, V, d, and p. In spite of the great current density differences for various values of D, and for little change in V, the equation

$$d = \frac{\mathrm{B}}{\sqrt{\mathrm{I}_s}} + \frac{\mathrm{A}}{\mathrm{P}}$$

---

* A. Gunther-Schulze, *Zeit. für Physik*, xix. p. 328 (1923).

is in agreement with all values of d_s and I_s in these experiments. Owing to the "hetero-normal" discharge, the constants B and A are capable of fairly accurate measurement with rough apparatus. The relation between d_s and I_s will, however, be left over for a future paper, because of the intimate connexion between the relation as obtained experimentally and that looked for on the basis of the various space-charge equations that have been applied to the discharge at the cathode.

AN EXPLANATION OF THE "HETERO-NORMAL" EFFECT.

It is recognized that the boundary of the C.D.S. and the negative glow is a region in which positive ions predominate. Thus, the recent work by Compton, Turner, and McCurdy * (in which Langmuir's † method was used for the determination of the ion concentration etc.) indicated that the electron concentration at the anode side of a particular negative glow was 101, and the positive ion concentration 51: corresponding concentrations at the middle of the same negative glow were 130 and 900 respectively. Let us assume that there is a layer of maximum concentration of positive ions near, or at, the boundary of the negative glow, and that the current through the C.D.S. is carried for the main part by positive ions. Then at any particular value of the cathode fall of potential, the total current across the C.D.S. can be increased in two ways:—(1) The positive ions at the layer of maximum concentration might be initially at rest in one case; and in the case of the current-increase might have initial velocities, thus facilitating movement of positive ions across the C.D.S. (2) Or, the region of maximum concentration of the positive ions might be moved as a whole nearer to the cathode surface. These two ways might be one and the same, and they amount to the same thing, an increase in the current carried across the C.D.S.

Now in order that the large density of ionization can be maintained at the negative glow, electrons, falling from the cathode surface region, are assumed to cause ionization by collision with the gas molecules in the negative glow region. The ions that are so produced commence life in a region of very small field intensity, and the positive ions, in particular, will not move far from their initial position of production before they are the victims of recombination. The efficiency

---

* Compton, Turner, & McCurdy, Phys. Rev. xxiv. p. 597 (1924).

† I. Langmuir, General Elec. Rev. 1923, p. 731.

of the electrons that produce positive ions in the negative glow region must therefore be small. If, however, an electron passing from the cathode surface penetrates the C.D.S. of an opposing cathode surface, such as we might assume in the case of the discharge between equipotential plates in the "hetero-normal" condition, the ions that are produced by collision with the gas molecules are initially in a region of strong electric field, and the positive ions will immediately begin their movement towards the cathode surface in the C.D.S of which they are produced. These positive ions will thus not be such easy victims of recombination : the efficiency of the electrons for effective production of positive ions is therefore at a maximum when the ionization takes place in the C.D.S. An effect of this kind would explain the "hetero-normal" condition, both as regards the current increases and the cathode fall of potential decreases. The region of maximum concentration of positive ions would, in effect, be moved nearer to the cathode surface, so that it is possible for a larger number of positive ions to reach the cathode surface. Or, the required current density can be carried at a smaller cathode fall of potential because of the initial velocities of the positive ions.

In the paper mentioned above, Schüler* explains the same effect that occurs in the inside of a cylindrical cathode as a result of the "Prinzip des kleinsten Zwanges."

PHENOMENA AT A HOLE IN A CATHODE.

The "hetero-normal" effect is germane to part of the phenomena described by Prof. M. E. Hufford†. The paper gives :—(*a*) A study of the discharge of electricity between parallel and equipotential plates which form the cathode of a discharge tube (see Plate xxxiv., *loc. cit.*). Experiments were made with different cathode materials, gases, and sizes of hole in the cathode, and the following characteristics were reported :—(*b*) The presence of a "bright bead" passing through the hole. (*c*) A glow filling the volume between P and P′. (See fig. 1, Hufford, *loc. cit.*)

(*a*) Hufford's discharge tube cannot be used to examine the discharge between equipotential plates over the range of pressures giving the "hetero-normal" effect. With the opposing cathode plates 4·8 cm. apart, gas pressures giving "normal" thicknesses of the order 2·4 cm. must be obtained before the "hetero-normal" effect becomes evident, and at the required pressure it is not possible to have a discharge between P, P′. From the point of view of experimental work on the discharge between equipotential plates, the Hufford type of tube is unnecessarily complex.

---

* Hermann Schüler, *Zeits. für Physik*, xxxv. No. 5, p. 324 (1926).

† Prof. M. E. Hufford, Phil. Mag. vol. l. No. 300, p. 1197 (1925).

(*b*) THE "BEAD."—Consideration of Hufford's results, and my own experiments with tubes such as those used by Hufford, indicate that there are two groups of phenomena at the hole in plate P.

(i.) There is "hetero-normal" or "hetero-abnormal" discharge from the wall and edge of the hole, resulting as it were in a foundation of negative glow in the hole;

(ii.) A second glow, superimposed upon the first, with characteristics that are those of positive column striations in the same discharge tube.

In Hufford's tube glow (i.), particularly at high pressures, often exists independently of glow (ii.) (examples are given on page 1211*). The resistance of the kind described above for the U-cathode is overcome at the hole by the negative glow due to discharge from the wall of the hole, and discharge to the inner space between P, P′ is the result. Glow (ii.) can be obtained at any similar constriction in the path of the Faraday Dark Space, or the negative glow. Thus, if P is disconnected from P′, and only P′ is used as cathode, the usual anode being retained, glow (ii.) is obtained at the hole in P. Thus the necessary overcoming of the resistance at the hole might conceivably be obtained as a result of the negative glow, or the glow (ii.). Glow (ii.) can exist in the hole without the discharge passing in the space PP′. Hence it is suggested that these experimental peculiarities, together with the results given by Hufford, concerning the pressures at which the bead appears and disappears in different gases, the dependence of the occurrence of the bead on the size of the hole, the current characteristics etc., point to the fact that some part of the phenomena at the hole has its explanation in the "hetero-normal" effect.

The superimposed glow gives three characteristics of the bead, namely, its round bead-like end (always turned away from the anode), its not infrequent striated nature, and much of its brightness; its occurrence and shape through and in front of the hole are generally determined by the "hetero-normal" or "hetero-abnormal" glow on which it is presumed to lie.

An examination of Hufford's graph fig. 3, p. 1202, showing results for the current passing to each of the plates P and P′ confirms that the bead has a foundation of negative glow. No matter what the pressure, a definite current density is demanded for a given thickness of the C.D.S., and assuming that a minimum thickness of the C.D.S. must be obtained before it is possible for the bead condition to exist at the hole, it follows that a certain definite current density is similarly required. From Hufford's graph it is seen that the total current through the tube is approximately constant over the range of pressure 0·70 to 0·25 mm. Hg (for air), and that for the same range the current to plate P is nearly constant at 8·5 milliamperes.

---

* *Loc. cit.* Hufford.

The currents used by Hufford to give the bead effect are all strongly "abnormal." For purposes of comparison it would have been an advantage had "normal" currents been used. It is apparent that the maximum pressure at which the bead will occur depends upon whether or not the "normal" discharge condition is maintained at each value of the pressure, because the maximum thickness of the C.D.S. at any pressure is the "normal" one, and the foundation of the bead is a result of the "overlapping" of the C.D.S.'s. of opposing cathode surfaces. With small holes, the "hetero-normal" effect appears for "abnormal" values of the current to P. Hufford's table I.* gives the range of pressures over which the bead can be maintained for an aluminium cathode, and hole 2·6 mm. diameter. Now the pressures at which the C.D.S. is 1 cm. in length, when unit current is flowing ($i=10^{-4}$ ampere per sq. cm.) are :— 0·70, 0·47, and 0·11 mm. Hg for helium, hydrogen, and air respectively : for these three gases therefore the "hetero-normal" effect would appear at a particular hole in the order : helium at the highest pressure, hydrogen at a lower pressure, and air at the lowest pressure. Assuming a minimum value of the pressure at which the bead can exist at the hole (of the nature of the minimum that is obtained for the U-cathode near the pressure 0·02 cm. Hg), the minimum pressure at which the bead should occur in the same three gases follows the same order, helium at the highest pressure, hydrogen at a lower, and air at the lowest pressure of the three. In general, for a particular hole, gases having the greater "normal" C.D.S. thickness pass as a bead at a higher pressure than gases having the smaller C.D.S. thickness. These considerations of the C.D.S. thickness applied to the condition for the "hetero-normal" effect to occur in a particular hole give the same results as were obtained experimentally by Hufford.

---

* *Loc. cit.* p. 1200.

The bead should appear and disappear at a lower pressure for the hole of larger diameter. The value 0·42 on p. 1203* is probably in error (see Table I. p. 1200), but the pressures given by Hufford at which the bead disappears (in the same table on p. 1203) follow the expected order. Again the values of the maximum pressures at which the bead effect occurs should be given for "normal" currents so that the results are strictly comparable.

The question of whether the "hetero-normal" and the "positive column glow" can exist together, or whether the "positive column glow" suppresses the "hetero-normal" one, cannot be completely answered from the above considerations, and an ultimate test will require the measurement of the current passing to the wall of the hole, apart from that passing to the surface of the plate P. A future paper, it is hoped, will deal with this question, together with the potential measurements reported by Hufford.

I am indebted to Prof. G. W. Todd, of Armstrong College, under whose supervision the experiments were carried out, and to the Department of Scientific and Industrial Research for the grant which has enabled me to undertake the work.

XLIX. *The Milner and Debye Theories of Strong Electrolytes.* *By* GEORGE SCATCHARD †.

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 178.)

IN a recent paper of this Journal, Pike & Nonhebel and Nonhebel & Hartley ‡ have published comparisons of the Milner and Debye theories, with conclusions very unfavourable to the latter. On account of the emphasis now being placed upon solutions of strong electrolytes, it seems desirable to show that the experiments of these authors do not necessarily lead to their conclusions.

Since both of these theories explain the deviations from the laws of ideal solutions, their exact forms depend upon the definition of the ideal solution. If this is defined as one in which the activity of each component is proportional to its mole fraction, the equation of Debye and Hückel becomes

---

* *Loc. cit.* p. 1200.

† Communicated by the Author.

‡ Pike & Nonhebel, Phil. Mag. vol. 1. p. 723 (1925); Nonhebel & Hartley, *ibid.* p. 729.

$$-\log\gamma = \frac{A\sqrt{2c}}{1+\alpha\sqrt{2c}} - B2c + \log(1+0{\cdot}002mw_1), . \quad (1)$$

in which γ is the ratio of the activity, a, to the molality, m, in moles of electrolyte per kilogram solvent; c is the concentration in moles per litre; for a uni-univalent electrolyte at 25°, A is equal to $249{\cdot}4/D^{\frac{3}{2}}$ ($D =$ dielectric constant of solvent); in the same case α equals $2{\cdot}06\times 10^8 b/D^{\frac{1}{2}}$ ($b =$ mean diameter of collision sphere of the ions, in centimetres); B is a complicated function of the temperature, ionic size, dielectric constant of the solvent and rate of change of the dielectric constant with changing electrolyte concentration.

Equation (1) contains two constants, α and B, which can be determined only approximately by independent measurements. Moreover, expansion of the first term on the right-hand side in a power series of c shows that the two are differentiated only in the coefficients of the three-halves and higher powers of c. So the equation may be simplified in dilute solutions. In the case of solvents of low dielectric constants, such as the alcohols, the term $B2c$ may be omitted, and the only effect will be to make the value of b calculated from α somewhat too large. In more dilute solutions the equation approaches

$$-\log f = A\sqrt{2c} - B'c, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which $f = a/c$ and B' is a new constant. At zero concentration the equation approaches

$$-\log f = A\sqrt{2c}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The formula of Milner cannot be expressed analytically. It gives the same values for all electrolytes of the same valence type, and values which do not differ very much from two-thirds those calculated from equation (3).

Nonhebel and Hartley compare the two theories with the experimental measurements of electromotive force of hydrochloric acid cells in water, ethyl alcohol, and methyl alcohol. They find that the Milner formula gives approximate agreement and that the Debye theory is much less satisfactory. In testing the Debye theory, however, they use equations (2) and (3) instead of equation (1). I have discussed elsewhere[*] the comparison of the complete theory of Debye and Hückel with the experimental measurements in water, in ethyl alcohol, and in their mixtures, and found the agreement to be excellent. So the present discussion may be limited to the new measurements in methyl-alcohol solutions. Attention should be called, however, to the solubility measurements of Brönsted and La Mer[†], which agree very closely with the Debye theory, but not at all with that of Milner.

Nonhebel and Hartley first test the two theories by the constancy of the quantity E_0, which may be defined by the equation

$$E_0 = E + 0{\cdot}1183\,(\log c + \log f) = E - 0{\cdot}0123 + 0{\cdot}1183\,(\log m + \log \gamma), \quad . \quad . \quad . \quad . \quad (4)$$

in which $-0{\cdot}0123$ is equal to $0{\cdot}1183\,(\log c - \log m)$ for methyl alcohol at 25°, and E is the measured electromotive force. In their test of the Debye theory, $\log f$ is determined from equation (3). They later compare f, calculated by equation (2), with the values computed from the experimental measurements and the value of E_0 determined by the use of Milner's formula. Both tests are inconclusive, because Debye's theory is not represented by either of these equations through the concentration range of the experimental measurements; the second method also uses a quantity determined by the use of one theory in the test of another theory incompatible with the first.

The combination of equations (1) and (4), with insertion of the proper values for methyl alcohol ($D = 30{\cdot}2$), gives

$$E_0 = E - 0{\cdot}0123 + 0{\cdot}1183\,[\log m - \log(1 + 0{\cdot}064\,m)] - \frac{0{\cdot}1767\sqrt{2c}}{1 + \alpha\sqrt{2c}} + B2c. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The values of c were computed by me from the approximate equation

$$c = \frac{m}{1{\cdot}2716 + 0{\cdot}02m}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If B be given the value zero, which is justifiable in the concentration range studied, the experimental data are best fitted with $\alpha = 1{\cdot}74$. Table I. and fig. 1 give the test of equation (5) and the comparison with the Milner formula.

---

[*] Journ. Am. Chem. Soc. xlvii. p. 2098 (1925).

[†] Brönsted & La Mer, Journ. Am. Chem. Soc. xlvi. p. 555 (1924).

In Table I. the first column gives the values of m; the second the values of E_0 computed by Nonhebel and Hartley with Milner's formula; the third the deviations of the values of the second column from the value of E_0 accepted by these authors; the fourth column contains the values of E_0 computed from equation (5); and the fifth gives the deviations of the values of the fourth column from their average, −0·0226 volt. Fig. 1 shows the same results graphically. It differs from fig. 2 of Nonhebel and Hartley in that it extends to higher concentrations and in that the ordinates are shown on a ten times larger scale. No attempt is made to draw curves through the points. Instead, the two accepted values of E_0 are represented by horizontal dotted lines.

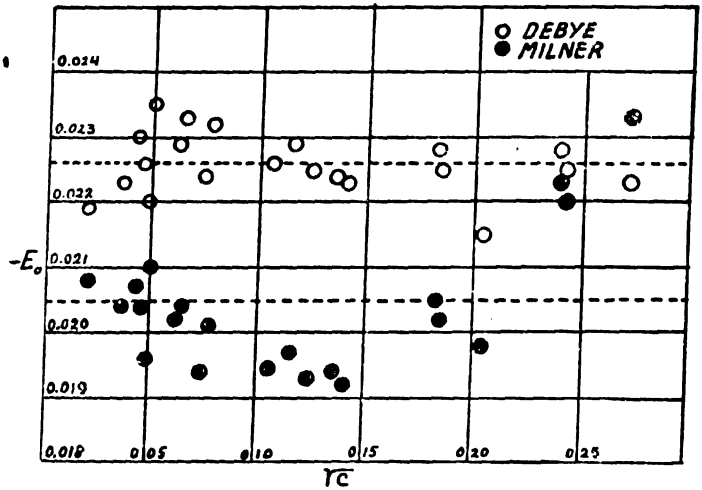
Table I.

Electromotive Force in Methyl Alcoholic Hydrochloric Acid at 25°.

	Milner.		Debye.	
m.	$-E_0$.	$-E_0-0{\cdot}0205$.	$-E_0$.	$-E_0-0{\cdot}0226$.
0·0004955	0·0208	+0·0003	0·0219	−0·0007
0·001652	0·0204	−0·0001	0·0223	−0·0003
0·002363	0·0207	+0·0002	0·0230	+0·0004
0·002683	0·0204	−0·0001	0·0226	0·0000
0·002980	0·0196	−0·0009	0·0220	−0·0006
0·003161	0·0210	+0·0005	0·0235	+0·0009
0·004939	0·0202	−0·0003	0·0229	+0·0003
0·005425	0·0204	−0·0001	0·0233	+0·0007
0·007113	0·0194	−0·0011	0·0224	−0·0002
0·009857	0·0201	−0·0004	0·0232	+0·0006
0·01444	0·0194	−0·0011	0·0226	0·0000
0·01722	0·0197	−0·0008	0·0229	+0·0003
0·01986	0·0193	−0·0012	0·0225	−0·0001
0·02363	0·0194	−0·0011	0·0224	−0·0002
0·02549	0·0192	−0·0013	0·0223	−0·0003
0·04261	0·0205	0·0000	0·0228	+0·0002
0·04356	0·0202	−0·0003	0·0225	−0·0001
0·05312	0·0198	−0·0007	0·0215	−0·0011
0·07332	0·0223	+0·0018	0·0228	+0·0002
0·07333	0·0223	+0·0018	0·0228	+0·0002
0·07507	0·0220	+0·0015	0·0225	−0·0001
0·09467	0·0233	+0·0028	0·0223	−0·0003
0·1155	...	...	0·0229	+0·0003
0·4802	...	...	0·0234	+0·0008
0·5574	...	...	0·0224	−0·0002

It is obvious from either the table or the figure that the complete Debye equation gives an E_0 value more constant than the Milner formula. Not only is the average deviation smaller, even up to 0·04 M, but there is no trend in the deviations, and the equation holds equally well up to the highest concentrations measured, which are ten times those at which the Milner formula begins to deviate seriously. It is also apparent that E_0 calculated from the Debye equation is as constant as the consistency of the experimental data warrants, and $-0·0226$ volt may be taken as the most probable value for E_0. It may be concluded that these measurements, considering the enormous difficulties of precise measurement in very dilute alcoholic hydrochloric acid, offer very good confirmation of the Debye theory.

Fig. 1.



From the value of 1·74 for α, the mean diameter of the collision spheres is $4·65 \times 10^{-8}$ cm. Other values for hydrogen chloride are: $4·05 \times 10^{-8}$ in water, $4·06 \times 10^{-8}$ in 50 mole per cent. ethyl alcohol, and $4·57 \times 10^{-8}$ in ethyl alcohol *. Since the value in methyl alcohol is somewhat too large on account of the change in dielectric constant being neglected, the agreement is very satisfactory.

I have shown how the radius of the electrification sphere can be calculated from the E_0 values in different solvents with the assumption that all the deviation from ideality is due to the electrical work. To account for the behaviour

---

* Scatchard, *loc. cit.*

of hydrochloric acid in alcohol-water mixture, it was suggested that this size might change from 5 to 4×10^{-8} cm. between 50 and 95 mole per cent. alcohol. From these measurements in methyl alcohol and those of Danner in ethyl alcohol a value of $3{\cdot}0 \times 10^{-8}$ may be calculated. The calculation is not very accurate, because the difference in dielectric constants and between electrode potentials in terms of mole fractions are both very small. Since any change in size is to be attributed largely to the reaction $H_2C^+ = H^+ + H_2O$, the change between 95 and 100 mole per cent. might well be as great as that between 50 and 95 mole per cent. Considering the breadth of the assumptions and the large effect of a small experimental error the agreement is quite satisfactory.

The Milner Formula.

Although Milner and Debye start with the same fundamental theorems of electrostatics and statistical mechanics, the results they obtain do not agree quantitatively. Milner states that "It may be shown that, as an approximation, and when h * is very small" the value of the virial of the ions is 1·253, or $\sqrt{\frac{\pi}{2}}$, that given by the limiting law of Debye, equation (3). Yet when h has the value corresponding to a concentration of 0·0001 M for a uni-univalent electrolyte in water at 0°, his virial is only 0·734 that of the equation (3), and the ratio decreases only to 0·656 in 0·2 M solution †. Most of this discrepancy may be attributed to inaccuracy in the Milner results. Milner himself continually refers to them as approximate. It seems probable that all his values are obtained by interpolation from the three values given in his first paper ‡. These results are obtained by graphic extrapolation from fifteen to infinity. To decrease substantially the range of extrapolation would require an amount of computation several thousand times that performed by Milner. It is worth while then to re-examine his method of extrapolation.

Since Milner's tables include data for only one of the three pairs of curves, his curves cannot be replotted accurately. Fig. 2, however, was obtained photostatically without serious distortion. To quote Milner again, "The extrapolation of these curves to the axis is certainly a rather violent one, but it may be done with some confidence by observing the following points :—(1) The first curve must be everywhere below the limit and the second one everywhere above it ; (2) the two curves must extrapolate to the same point on the axis ; (3) from the fact that the virial of the ions external to the second arrangement is zero, it may be inferred that the second curve for large values of m * approaches the limit much more closely than the first one, and that it probably tends to become parallel to the axis as $m^{-\frac{1}{3}}$ becomes zero."

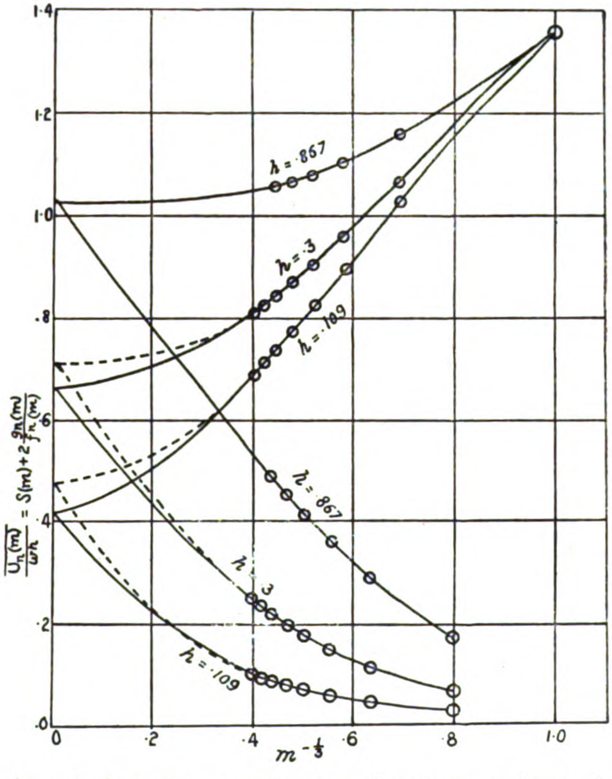
---

* h is a function of the ionic charge, the dielectric constant of the solvent, the temperature, and the concentration. By Milner's theory the virial is equal to $RThf(h)$.

† A. A. Noyes, Journ. Am. Chem. Soc. xlvi. p. 1080 (1924).

‡ Milner, Phil. Mag. xxiii. p. 551 (1912).

Fig. 2.



Inspection of fig. 2 shows that the dotted lines fulfil these conditions, especially the third, even better than do the full lines which represent Milner's extrapolation. The

---

* m is the number of ions whose effect on the virial is counted.

lowest pair might equally well be extrapolated to a still higher value. The results of the two extrapolations and the value of the Debye limiting law, equation (3), are given in Table II. The last two columns show the corresponding concentration of a uni-univalent electrolyte in water at 0° and in methyl alcohol at 25°. The most important conclusion to be drawn is that the Milner theory does not lead necessarily to the Milner formula, but may equally well give higher values for the slope. The values in the third column of Table II., which are shown in fig. 2 to be consistent with the Milner theory, were computed from the equation

$$f(h)=\frac{\sqrt{3h}}{1+0{\cdot}35\sqrt{3h}}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which at small concentrations must approach the Debye limiting law, which corresponds to $f(h)=\sqrt{3h}$.

TABLE II.

$f(h)$ of Milner's Theory.

h.	$f(h)$. Milner.	$f(h)$. Eq. 4.	$f(h)$. Debye ($\sqrt{3h}$).	C_{H_2O}.	C_{MeOH}.
0	0	0	0	0·0	0·0
0·109	0·42	0·48	0·57	0·0007	0·00004
0·3	0·66	0·71	0·95	0·015	0·00085
0·867 *	1·03	1·03	1·61	0·562	0·0206

There must, however, be a discrepancy between the results of Milner and the limiting law of Debye at finite concentrations, a discrepancy which increases with increasing concentration. There are two possible explanations: both methods give only approximations of the virial, the approximations may not be exactly the same; both methods consider the size of the ions in the early stages but ignore the size later, and the exact stage at which the size of the ions is ignored may influence the effect so that, relative to equation (3), the Milner theory may make a partial correction for ionic size. It would be an extremely tedious task to settle these points for the Milner theory. The Debye theory, on the other hand, is so direct in its development that the approximation may be improved at any time by including more terms in the series used to approximate the

---

* To quote Milner again: "This value of h is so large that the expression for the virial obtained in this paper would no longer be valid."

Boltzmann equation. It already gives a method for taking into account the size of the ions, and may readily be made more accurate in this respect whenever there is discovered a law for the repulsive forces between atoms more accurate than the rigid-sphere assumption.

The Determination of Free Energies from the Mutual Potential Energies of the Ions.

Pike and Nonhebel criticize the method of calculating the free energy from the mutual potential energy of the ions by an equation of the Gibbs-Helmholtz type, and claim that it cannot lead to quantitative results. Much of their argument is an attack on an equation of Debye and Hückel, given on page 725 between equations (10) and (11). This equation does not follow from the Debye theory without additional assumptions, and it is thermodynamically incompatible with the Debye theory for the free energy of the solutions. Although the equation is undoubtedly incorrect, that fact cannot effect the validity of the Debye theory.

Gross and Halpern[*] have given a justification of the method used by Milner and by Debye and Hückel, in which the relation between the mutual potential energy of the ions and the free energy of the solution is obtained by using the *partial* derivative of the free energy with respect to the temperature. They have also shown that the relation between the total internal energy of the solution and the free energy, for which the thermodynamics requires the *total* derivative with respect to the temperature, shows at least approximate agreement between the Debye theory and thermal measurements if the size of the ions varies slightly with the temperature.

Another confirmation of the exactness of this method is obtained from the fact that the same result has been obtained by three other methods, none of which depend on an integration with respect to the temperature. The first of these, used by Milner and by Nonhebel and Hartley, is to take the osmotic pressure as equal to the virial. The second, given by Noyes[†], calculates the vapour-pressure of the ions from kinetic theory. These two are applicable only in dilute solutions. The third method[‡] makes use of the difference in electrical work of charging the ions reversibly in the solution in question and in an infinitely dilute solution It may be applied to solutions of any concentration.

---

[*] Gross & Halpern, *Physikalische Zeitschrift*, xxvi. p. 403 (1925).
[†] Noyes, *loc. cit.*
[‡] Debye, *Physikalische Zeitschrift*, xxv. p. 97 (1924).

Gross and Halpern[*] object to this last derivation on the grounds that the potential of any individual ion oscillates rapidly about the mean potential. This objection could be met by the invention of a device which would prevent the discharging of an ion and permit its charging only when its potential and charge each differ from the average by less than some infinitesimal amount. Such a device would increase the order of infinity of the time of the charging process, but that is unimportant in a purely theoretical process, in which the question of practical realizability is irrelevant.

The application of thermodynamic criteria to this step of the derivation is entirely beside the point, since one quantity involved—the mutual potential energy of the ions—cannot be represented by any of the ordinary thermodynamic equations; for these equations are incapable of dividing energy between the components of a phase. The final results may be tested thermodynamically by the application of the ordinary equations. In all tests so far made of the Debye theory, an agreement at least approximate has been found.

Cambridge, Massachusetts.

L. *The Milner and Debye Theories of Strong Electrolytes.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

OUR disagreement with Dr. Scatchard (*suprà*, p. 577) with regard to the activity coefficients of hydrogen chloride in methyl-alcohol solutions lies in the choice of the constant E_0 in the equation $E = E_0 - 0{\cdot}1183 \log cf$. The value of E_0 can be obtained without any theoretical assumptions by plotting $E_0' = E + 0{\cdot}1183 \log c$ against the square root of the concentration. The values of E_0' for hydrogen chloride in methyl alcohol are found to lie on a straight line within the limits of experimental error up to a concentration of 0·01 N, and they give a value for E_0 of $-0{\cdot}0205$ volt. It was hoped that this quantity would be obtained more accurately by using the limiting equations of Milner and Debye in the manner described in our paper (Phil. Mag. (6) vol. l. p. 729, 1925). Dr. Scatchard has obtained the value $E_0 = -0{\cdot}0226$ volt by making use of the complete Debye equation and adjusting the value of the mean diameter of the collision sphere of the ions until a constant value for E_0 was obtained. The figure on page 739 of our paper shows that this value is incompatible with the extrapolation of E_0'.

---

[*] Gross & Halpern, *loc. cit.*

The constancy of E_0 values calculated from experimental results at higher concentrations, using the Debye equation, does not seem to us a sufficient reason for taking a value for E_0 which is inconsistent with the experimental results in less concentrated solutions.

We have been in correspondence with Professor Milner, and with his permission quote the following paragraph from his letter :—"Since I have read Debye's calculation critically, I think that his method of calculation of the effects of interionic force is greatly superior to mine. All the laborious summations and approximations contained in my calculation of 1912 are done away with, without any sacrifice of accuracy, by what seems to me a stroke of genius—namely, his observation that the average potential at a point of all the ions in a sphere containing a positive ion at the centre must satisfy Poisson's equation. Since the two calculations are based on the same assumptions and mine contains admitted approximations, I am inclined to believe that the numerical differences between them are to a large extent attributable to these. At any rate, I think this is the case with regard to the $\sqrt{\frac{\pi}{2}}$ ratio, by which the limiting values of the internal energy at $h=0$ differ. In my footnote on this matter I said, 'It may be shown that, *as an approximation*, and when h is very small, $\overline{U} = -wh\sqrt{\frac{3\pi}{2}h}$.' The statement was put in that form because it was clear to me that the coefficient was only an approximation even in the limit. The result was obtained, in fact, by a method which assumed that expressions for the average effect of all groups on the next ion outside them could be replaced by similar expressions for the effect of a group containing the average charge of the previously-mentioned groups. An assumption of this kind will only give an approximate result for the *coefficient* even in the limit when $h=0$, although the nature of the function would not be affected."

Yours faithfully,
G. Nonhebel, B.A.,
H. Hartley, M.A.

Balliol College, Oxford.
April 28, 1926.

LI. *On a Geometrical Presentment of the Constants of an Elastic Material.* *By* R. F. GWYTHER, *M.A.**

IN this paper I propose to construct the general expression for the potential function of strain per unit of volume in a material, on the assumption that the strain is small and that the material acts under strain as a conservative system. There is a further question, not here considered, as to whether the resulting stresses are such as can satisfy the mechanical stress equations.

The potential function will be a quadratic function of the six elements of strain, and it must possess permanency of form for any transformation of the coordinate axes, or must be an invariant quadratic function. It must also be positive for all small values of the elements of strain.

1. The general method which I employ here, as I have employed elsewhere, is an adaptation of the method of Differential Invariants and Covariants of Curves and Surfaces to apply to vectors, stresses, strains, etc., instead of purely geometrical subjects.

Imagine a small rotation of the coordinate axes about their own positions indicated by ω_1, ω_2, ω_3 respectively, the material remaining stationary.

In consequence of this rotation, of which the components may be considered separately, there will be an alteration in the expressions considered which will depend upon their nature—as vectors, stresses, strains, and so forth. Generally, quantities showing similar characteristics will, on transformation of coordinate axes, alter in the same manner.

I shall employ Ω_1, Ω_2, Ω_3 (which will be differential operators) to indicate the change consequent upon the rotations ω_1, ω_2, ω_3 respectively, and their expressions will be found by forming the coefficients of ω_1, ω_2, ω_3 respectively in the complete change. These operators will be distinctive in form for quantities of different kinds.

For example:

$$x \text{ will change to } x+\omega_3 y-\omega_2 z, \text{ etc.};$$

$$u \text{ will change to } u+\omega_3 v-\omega_2 w, \text{ etc.};$$

$$\frac{\partial}{\partial x} \text{ will change to } \frac{\partial}{\partial x}+\omega_3\frac{\partial}{\partial y}-\omega_2\frac{\partial}{\partial z}, \text{ etc.};$$

$$\frac{\partial u}{\partial x} \text{ will change to } \frac{\partial u}{\partial x}+\omega_3\left(\frac{\partial u}{\partial y}+\frac{\partial v}{\partial x}\right)-\omega_2\left(\frac{\partial u}{\partial z}+\frac{\partial \omega}{\partial x}\right), \text{ etc.} \quad . \quad . \quad . \quad (1)$$

---

* Communicated by the Author.

Hence, acting on a vector (u, v, w) or (x, y, z),

$$\Omega_1 = w\frac{\partial}{\partial v} - v\frac{\partial}{\partial w}, \quad \Omega_2 = u\frac{\partial}{\partial w} - w\frac{\partial}{\partial u}, \quad \Omega_3 = v\frac{\partial}{\partial u} - u\frac{\partial}{\partial v};$$

$$\Omega_1 = z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}, \quad \Omega_2 = x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}, \quad \Omega_3 = y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}. \quad . \; . \; . \quad (2)$$

Taking the elements of strain from (1) and (2), we find

$$\Omega_1 = a\left(\frac{\partial}{\partial f} - \frac{\partial}{\partial g}\right) + 2(g-f)\frac{\partial}{\partial a} - c\frac{\partial}{\partial b} + b\frac{\partial}{\partial c}. \quad . \; . \quad (3)$$

The expressions for Ω_2 and Ω_3 may be written down by a cyclic interchange.

As a further example, which I shall make use of later, write

$$X = a^2 - 4fg, \qquad Y = b^2 - 4eg, \qquad Z = c^2 - 4ef,$$
$$\xi = 4ae - 2bc, \qquad \eta = 4bf - 2ac, \qquad \zeta = 4cg - 2ab;$$

by using (3), we shall find

$$\Omega_1 = \xi\left(\frac{\partial}{\partial Y} - \frac{\partial}{\partial Z}\right) + 2(Z-Y)\frac{\partial}{\partial \xi} - \zeta\frac{\partial}{\partial \eta} + \eta\frac{\partial}{\partial \zeta}, \quad . \quad (4)$$

which reproduces the form of (3).

If, again, we write

$$X = x^2, \quad Y = y^2, \quad Z = z^2, \quad \xi = 2yz, \quad \eta = 2zx, \quad \zeta = 2xy,$$

we again find

$$\Omega_1 = \xi\left(\frac{\partial}{\partial Y} - \frac{\partial}{\partial Z}\right) + 2(Z-Y)\frac{\partial}{\partial \xi} - \zeta\frac{\partial}{\partial \eta} + \eta\frac{\partial}{\partial \zeta}, \quad . \; . \quad (5)$$

reproducing the form of (3) or (4).

2. If $Ax^2 + By^2 + Cz^2 + 2Dyz + 2Ezx + 2Fxy$, where x, y, z are the coordinates of a point in the material, is to be a co-variantal expression retaining permanence of form for any transformation of coordinates, then Ω_1, Ω_2, Ω_3 acting upon the terms in the expression must each produce a null result.

By making use of (5), we find that, acting on the coefficients only,

$$\Omega_1 = 2D\left(\frac{\partial}{\partial B} - \frac{\partial}{\partial C}\right) + (C-B)\frac{\partial}{\partial D} - F\frac{\partial}{\partial E} + E\frac{\partial}{\partial F}, \text{ etc.} \quad (6)$$

This is therefore the condition that

$$Ax^2 + By^2 + Cz^2 + 2Dyz + 2Ezx + 2Fxy = \text{constant} \quad . \quad (7)$$

should be the equation to a quadric traced in the material, and, retaining the same form in a change of coordinate system, may be called the equation to a covariant quadric.

On referring to (3), it will be seen that, under these conditions,

$$Ae+Bf+Cg+Da+Eb+Fc \quad . \quad . \quad . \quad . \quad (8)$$

is an invariant expression.

While from (4) it follows that

$$A(a^2-4fg)+B(b^2-4eg)+C(c^2-4ef) \\ +2D(2ae-bc)+2E(2bf-ac)+2F(2cg-ab) \quad (9)$$

is also an invariant expression.

It is desirable to note that if $\{P, Q, R, S, T, U\}$ are the elements of stress, the expression for Ω_1 when acting on these elements is

$$\Omega_1=2S\left(\frac{\partial}{\partial Q}-\frac{\partial}{\partial R}\right)+(R-Q)\frac{\partial}{\partial S}-U\frac{\partial}{\partial T}+T\frac{\partial}{\partial U}, \quad (10)$$

and is of the same form as (6). Accordingly, the coefficients $\{A, B, C, D, E, F\}$ in a covariant quadric act on transformation of coordinate axes as the elements of stress act, in spite of the difference in dimensions.

3. We may now proceed to make use of (8) and (9) to construct the general invariantal expression of the second degree in the elements of strain, and for this purpose I shall, in the first instance, give a geometrical aspect to the question.

Imagine four concentric ellipsoids to be traced in the material under strain, arbitrary both as to the magnitude and orientation of their principal axes. Indicate their equations relative to their principal axes by

$$\begin{aligned} \alpha_0x^2+\beta_0y^2+\gamma_0z^2 &= M_0, \\ \alpha_1x^2+\beta_1y^2+\gamma_1z^2 &= M\ , \\ \alpha_2x^2+\beta_2y^2+\gamma_2z^2 &= M\ , \\ \alpha_3x^2+\beta_3y^2+\gamma_3z^2 &= M\ , \quad . \quad . \quad . \quad . \quad (11) \end{aligned}$$

and their equations relative to arbitrarily chosen coordinate axes by

$$px^2+qy^2+rz^2+2syz+2tzx+2uxy = M, \quad . \quad (12)$$

with the proper subscript numbers in accordance with (11).

As the ellipsoids are fixed in the material, we may form invariantal expressions by using (8) and (9). From the first of the ellipsoids, I shall use (9) and obtain

$$p_0(a^2-4fg)+q_0(b^2-4eg)+r_0(c^2-4ef) \\ +2s_0(2ae-bc)+2t_0(2bf-ac)+2u_0(2cg-ab), \quad (13)$$

which I shall indicate by A_0.

This will form part of the invariant function of the second degree in strains which it is proposed to find.

As the ellipsoids are arbitrary, we shall be unable to increase the generality of the expression by adding a second invariant of the same character, for the sum would only amount to the substitution of one arbitrary invariant quantity for another.

From each of the other three ellipsoids we will form from (8) the invariant of the first degree,

$$p_1e+q_1f+r_1g+s_1a+t_1b+u_1c, \text{ etc.,}$$

which I shall indicate by B_1, B_2, and B_3 respectively. (14)

The general invariantal expression of the second degree is then

$$2V=A_0+B_1^2+B_2^2+B_3^2. \quad . \quad . \quad . \quad . \quad (15)$$

It will be seen that the argument I have used against repeating such a term as A_0 does not apply to B_1^2, etc.

This expression contains 24 coefficients or 24 apparent constants, but three of them are introduced by the arbitrary character of the coordinate axes.

As the first ellipsoid is, of necessity, specially treated in forming (15), we will suppose that the equations of the other ellipsoids are first transformed to the principal axes of the first ellipsoid and then to the arbitrary coordinate axes, in case that step is necessary.

But we shall have reduced the constants to 21, if we refer the equations of the four ellipsoids to the principal axes of the first. The coefficients will then contain the 12 coefficients in the equations of the four ellipsoids referred to their principal axes, and trigonometrical ratios of the three sets of three angles (conveniently the θ, ϕ, ψ employed in the Precession of the Equinoxes) which express the direction cosines of the principal axes of the last three of the ellipsoids referred to those of the first. This gives 12 dimensional constants, with the trigonometrical ratios of 9 angles, on which the 21 coefficients in the full expression for 2V depend.

4. The geometrical treatment which I have thought illuminating is not the only method which might be used.

If we take the equations of the four ellipsoids in the form given by (12) referred now to arbitrary coordinate axes, we may construct A_0, B_1, B_2, B_3 as in (13) and (14), and finally 2V as in (15) as before, and then proceed as follows:—By (9) and (10), the coefficients in A_0, B_1, etc., transform as the elements of stress transform, and may be expressed in terms of quantities corresponding to their principal or normal stress elements and the angles these normal elements make with the coordinate axes. We thus obtain an analysis similar to that obtained by the more geometrical method.

5. In the case of an isotropic material, we only need the first ellipsoid and one of the other three ellipsoids, and each of these two ellipsoids is to be a sphere, since the material is isotropic. Accordingly (15) becomes

$$2V = m(e+f+g)^2 + n(a^2+b^2+c^2-4fg-4eg-4ef) \quad (16)$$

in the usual form.

6. This paper does not deal with any physical aspect of the argument for reducing the number of elastic constants, but I think it throws light upon the discussion on the surfaces, based on the general expression for 2V, found by Haughton in 1846, and discussed by Rankine and Saint Venant *.

Indicating the terms in 2V by reference to the strain elements forming the several terms, we may write

$$2V = \lambda_{11}e^2 + 2\lambda_{12}ef + 2\lambda_{13}eg + 2\lambda_{14}ea + 2\lambda_{15}eb \\ + 2\lambda_{16}ec + \text{etc.}, \quad (17)$$

where, in the subscript numbers, 1 denotes e, 2 denotes f, etc., and $P = \frac{\partial V}{\partial e}$ etc.

The "tasinomic" quartic is formed by writing x^2 for e, y^2 for f, etc., in the expression for 2V, and the "orthotatic" ellipsoid is derived in the same way from the invariant P + Q + R.

These two surfaces are thus explained by the method of this paper. The other ellipsoid, named "heterotatic," is explained in a different manner.

The equation given for this surface is

$$(\lambda_{44}-\lambda_{23})x^2 + (\lambda_{55}-\lambda_{13})y^2 + (\lambda_{66}-\lambda_{12})x^2 \\ + 2(\lambda_{14}-\lambda_{56})yz + 2(\lambda_{25}-\lambda_{46})zx + 2(\lambda_{36}-\lambda_{45})xy = 1. \quad (18)$$

---

* I cannot give the references. I think they are to be found in Todhunter's 'History of Elasticity.'

The explanation is that, in accordance with (9),

$$(\lambda_{44}-\lambda_{23})(a^2-4fg)+(\lambda_{55}-\lambda_{13})(b^2-4eg)$$
$$+(\lambda_{66}-\lambda_{12})(c^2-4ef)+2(\lambda_{14}-\lambda_{56})(2ae-bc)$$
$$+2(\lambda_{25}-\lambda_{46})(2bf-ac)+2(\lambda_{36}-\lambda_{45})(2cg-ab) \quad (19)$$

is an invariant expression, and is an essential part of 2V. It is, in fact, that part of 2V, as expressed in (17), which I have denoted by A_0 in (15), and which certainly appears in the simple case of isotropy in (16).

The reduction of the number of constants is not to be found by making the coefficients in (18) and (19) null.

Kirkland, Newbiggin,
Carlisle.

LII. *Intensity Variations in the Spectrum of Neon.*

By Mary R. Johnson, *M.Sc., and* R. C. Johnson, *B.A., Ph.D., Department of Physics, Queen's University, Belfast* [*].

[Plate X.]

Introduction.

COMPARATIVELY little experimental work has been done in connexion with the distribution of intensity in line spectra and the variations which can be produced under different conditions. The reason for this is probably to be found in the absence, until very recently, of any theoretical work which might serve as a basis for the interpretation of the results, and perhaps also in the absence of precision methods at all comparable in accuracy with those available for the measurement of wave-lengths. Of the various experimental devices for measuring the intensities of spectral lines, those which are based on the use of a thermopile and galvanometer are subject to the serious difficulties involved in maintaining a source of light constant in output over a considerable time. Photographic methods, on the other hand, while involving the peculiarities of the photographic plate, provide a simultaneous record of the whole of the lines in a spectrum under identical conditions of production.

One simple mode of procedure consists in the use of a neutral tinted wedge of absorbing material mounted in front of the slit of a spectrograph. This reduces the photographed spectrum to a number of wedge-shaped lines of various lengths, and these lengths can be simply related to their "photographic" intensities. The theory of the neutral wedge has been largely developed by Merton and Nicholson [*], and was applied by them to a study of the line spectrum of helium under various conditions.

---

[*] Communicated by the Authors.

Another method is described by Ornstein[†] which consists in passing the light through a series of parallel strips of absorbing material of different densities before focussing on the slit of the spectrograph. This would really be equivalent to an echelon-shaped "wedge" of absorbing material in front of the slit. What is then measured is not the length of the spectrum line, but (by means of a registering micro-photometer) the density of the various elements composing it. A graphical method is then used to determine the photographic intensity of one line compared with another. In both these methods it is necessary to determine the variation with wave-length of the absorbing power of the strips (or the wedge), in order to render possible the comparison of spectral lines differing appreciably in wave-length.

In connexion with multiple spectral lines Ornstein and his co-workers have been able to show that the intensity ratios of the components are a well-defined specific property of the emitting atom,—independent of exciting conditions,—and they have framed general rules for the formulation of these results. These rules are applicable also to the Zeeman-patterns of lines, and they have a straightforward interpretation on the basis of the Quantum Theory.

There is, as yet, however, no theoretical or empirical formulation of the energy distribution in a line series or spectrum. There are indeed many serious difficulties in the way of any attempt to formulate such a theory on the basis of experimental work. These difficulties arise from the numerous factors: type of discharge, current density, pressure of gas, presence of other gases, etc., which are all capable of modifying to some extent the "normal" intensity distribution. With this in view Hughes and Lowe [‡] have investigated the line spectra of hydrogen and of helium as far as possible as a function of one variable, viz., the energy of impact of the exciting electrons. They found that a curve expressing the variation of intensity with the energy of the exciting electron was characteristic in its general form of a particular series; but even under these simple conditions there is no simple law apparent which could be formulated mathematically. The whole question of the intensity distribution in a line spectrum is therefore very complex, and for the present it would scarcely seem possible to do more than collect and compare data in the cases of some simple gases.

---

[*] Phil. Trans. A. vol. ccxvi. p. 459; vol. ccxvii. p. 237; vol. ccxx. p. 137.

[†] Proc. Phys. Soc. of London, vol. xxxvii. (5) p. 334 (1925).

[‡] Phys. Rev. vol. xxi. p. 292 (1923); Proc. Roy. Soc. A. vol. civ. p. 480 (1923).

The present investigation comprises a systematic record of the variations occurring in the spectrum of Neon. It was suggested originally by the exceptional variations of intensity of the line λ 5852, which had been observed visually during the course ot some work on the effects of Neon on the spectra of other substances with which it was mixed. The very conspicuous variations of this line led us to consider the desirability of an extensive investigation of the Neon spectrum, in the hope that if such effects occurred in this case in an exaggerated form we might be able to correlate them to the series classification of Paschen [*], and deduce some very general rules.

We have followed the experimental procedure of Merton and Nicholson and used a neutral tinted wedge throughout the work. We have also converted all our photographic intensities to absolute values by comparison with the radiation from the positive crater of the carbon arc (taken as black body radiation at an absolute temperature of 3750 degrees), following the method of these investigators in 1917. These absolute values have in each case been referred for convenience to that of λ 6402 as 100·0. Successive tables record the effects of current-density, condensed and "bulb" discharge, high and low pressure, admixture of hydrogen, argon, helium, and carbon dioxide, and the intensity distribution as a function of the distance from a flat cathode.

The whole of the results recorded in the present paper are for the visible spectrum only. It was originally intended to obtain a complete record for the ultra-violet also, by the use of a platinum wedge deposited on quartz as recommended recently by Merton [†]. A number of other things have so far prevented this, but it was felt desirable to record the fairly extensive work on the variations of the visible spectrum of Neon, deferring full discussion till they can be supplemented.

Reference to Paschen's papers shows that all the strong lines in the red, orange, and yellow (which constitute almost all the lines which could be photographed through the wedge used) are the first members of different principal series. The second and higher members are mostly below λ 3700. With the ordinary discharge and normal exposures only two diffuse lines and one sharp line appeared, and these were comparatively faint. It is therefore clearly impossible with the present data to discuss the intensity distribution along a series, or satisfactorily to compare the principal and subordinate series together. This must be reserved till ultra-violet measurements are available. In the present paper discussion is therefore chiefly limited to a comparison of the various principal series among themselves (as typified by their first members). For this purpose we have grouped together the various principal series having a common final term : $1{\cdot}5s_2$, $1{\cdot}5s_3$, $1{\cdot}5s_4$, $1{\cdot}5s_5$, etc., and this arrangement has been adhered to throughout the various tables.

---

[*] *Ann. der Phys.* vol. lx. p. 405 (1919): vol. lxiii. p. 201 (1920).

[†] Proc. Roy. Soc. A. vol. cvi. p. 378 (1924).

Experimental Detail.

The glass wedge employed was supplied by Messrs. Adam Hilger. The processes of calibration, *i.e.* the determination of the density gradient as a function of wave-length, were essentially the same as those described by Merton (*loc. cit.*). We have found that a tube filled with helium, when excited by an induction coil which was supplied with current from storage cells, is a reasonably constant source of light. For the process of reducing the light in a known ratio we have used copper foil perforated with circular holes by a punch. The optical density of these could be relied on to a high degree of accuracy. We found it convenient to use two such plates in the calibration of the neutral wedge (optical densities 0·4845 and 0·8216) for the weaker and stronger lines repectively. The "photographic" intensity of a line is related to the optical density of the wedge (d_λ), its height (h) on the plate, and the magnification (m) of the spectrograph by the formula:

$$I_{(\text{Photo.})} = \log_{10}{}^{-1} \frac{d_\lambda h}{m}.$$

This expression, of course, does not take into account the varying sensitivity of the photographic plate with wave-length. The conversion of photographic intensities to absolute values was done by multiplying by the factor

$$\left[\frac{\text{Absolute Intensity of Carbon arc}}{\text{Photographic Intensity of Carbon arc}}\right]_\lambda,$$

where the positive crater of the carbon arc was recorded on the same plate, and its photographic intensities were deduced from measurements of "h" for various wave-lengths. As already mentioned, the absolute radiation for a given wave-length was calculated from the formula of Wien :—

$$I_{\text{Abs.}}=\lambda^{-5}e^{-\frac{1\cdot445}{3750\lambda}},$$

taking the value for $\lambda=3888\,.\,10^{-8}$ cm. arbitrarily as unity (as suggested by Merton). The values were, of course, corrected for the dispersion of the spectrograph.

We found it possible to measure the heights of lines directly from the negatives taken. We used Ilford Rapid Process plates throughout, and "cut" these slightly with potassium ferricyanide so as to give a very sharp end point.

The effect of irradiation, which is large for the strong lines, was eliminated by arranging that the cross-wire of the measuring micrometer ran from the base of one very weak line to the base of another, in both of which the effect was apparently negligible. Allowing for these things any error in "h" is probably less than one per cent. for most lines. Assuming the process of "cutting" a subtractive one, as seems reasonable, the degree of cutting is immaterial so long as the wedge spectrum in question and the spectrum of which the absolute intensities are known are taken on the same plate, and therefore have the same subsequent treatment.

For

$$\frac{10^{-\frac{d_\lambda(h_1-x)}{m}}}{10^{-\frac{d_\lambda(h_2-x)}{m}}}=\frac{10^{-\frac{d_\lambda h_1}{m}}}{10^{-\frac{d_\lambda h_2}{m}}},$$

where x = amount cut off each line.

It is not, however, permissible to use the photographic intensities of the carbon arc from one plate in order to deduce the absolute intensities of the lines on another, even if taken from the same batch. For if h_1 = original height of a line of wave-length λ and h_2 = the corresponding height in the carbon arc, while x is the height cut off from the first and y from the second:

$$\frac{10^{-\frac{d_\lambda}{m}(h_1-x)}}{10^{-\frac{d_\lambda}{m}(h_2-y)}}=10^{\frac{d_\lambda}{m}(x-y)}\times\frac{10^{-\frac{d_\lambda}{m}h_1}}{10^{-\frac{d_\lambda}{m}h_2}},$$

so that the absolute value of the line in question is in error by the factor $10^{\frac{d_\lambda}{m}(x-y)}$. As all the lines are referred to some particular one, as 100 say, this error would be eliminated, but for the factor varying with d_λ through the spectrum, *e. g.* with the particular wedge used and assuming $x-y=\frac{1}{2}$ mm. say, the factor is 1·268 at λ 6717 and 1·481 at λ 4340.

The absolute values of the Neon lines in Table I. were deduced from a good plate on which the positive crater of the carbon arc was photographed in addition to the Neon

Table I.

Photographic and Absolute Intensities of Neon Lines.
(Uncondensed Discharge.)

Wave-length.	Abs. Int. of C. arc.	Photo. Int. of C. arc.	Abs./Photo. of C. arc.	Neon. Photo. Int.	Neon. Abs. Int.	Series.
7245	55·90	6·552*	8·53	0·55	84·3	$1{\cdot}5s_4-2p_{10}$
7174	54·09	11·09*	4·88	0·42	37·0	$1{\cdot}5s_2-2p_8$
7032	50 40	31·65*	1·59	4·45	127·2	$1{\cdot}5s_3-2p_{10}$
6929	47·75	66·73	0·715	6·29	80·9	$1{\cdot}5s_2-2p_6$
6717	42·31	210·8	0·201	12·55	45·4	$1{\cdot}5s_2-2p_5$
6678	41·33	254·1	0·163	20·14	59·1	$1{\cdot}5s_2-2p_4$
6599	39·38	357·6	0·110	17·70	35·0	$1{\cdot}5s_2-2p_2$
6533	37·74	449·2	0 0840	18·09	27·3	$1{\cdot}5s_3-2p_7$
6506	37·07	489·7	0·0757	45·06	61·4	$1{\cdot}5s_4-2p_8$
6402	34·62	622·4	0·0556	100·0	100·0	$1{\cdot}5s_5-2p_9$
6383	34·19	631·4	0·0542	48·37	47·2	$1{\cdot}5s_4-2p_7$
6334	33·02	663·6	0·0498	46·24	41·4	$1{\cdot}5s_5-2p_8$
6305	32·34	682·2	0·0474	20·06	17·1	$1{\cdot}5s_4-2p_6$
6266	31·45	716·4	0·0439	28 62	22·6	$1{\cdot}5s_3-2p_5$
6217	30·34	651·0	0·0466	17·35	14·5	$1{\cdot}5s_5-2p_7$
6182	29·38	680·1	0·0432	1·020	0·79	$2p_9-3{\cdot}5s_5$
6164	29·16	694·9	0·0420	19·34	14·6	$1{\cdot}5s_3-2p_2$
6143	28·69	714·2	0·0402	47·69	34·5	$1{\cdot}5s_5-2p_6$
6096	27·68	722·8	0·0383	34·99	24·1	$1{\cdot}5s_4-2p_4$
6074	27·20	687·9	0·0395	27·23	19·4	$1{\cdot}5s_4-2p_3$
6030	26·16	645·5	0·0405	9·82	7·16	$1{\cdot}5s_4-2p_2$
5992	25·22	585·7	0·0431	0·58	0·45	$2p_6-4d_1$
5988	25·22	585·7	0 0431	0·58	0·45	$2p_6-4d_3$
5975	25·10	557·5	0·0450	8 06	6·52	$1{\cdot}5s_5-2p_5$
5945	24·47	533·3	0·0459	23·31	19·2	$1{\cdot}5s_5-2p_4$
5902	23·61	474·2	0·0411	1·44	1·07	$2p_4-3{\cdot}5s_1$
5882	23·17	444·8	0·0521	13 29	12·5	$1{\cdot}5s_5-2p_2$
5852	22·62	415·5	0·0544	41·75	40·9	$1{\cdot}5s_2-2p_1$
5820	21 98	375·8	0·0585	1·06	1·12	$2p_5-4d_4$
5804	21·66	358·5	0·0604	0·44	0 48	$2p_8-4d_1$
5764	20·88	317·4	0·0658	1·49	1·76	$2p_9-4d_1$
5748	20·56	300·9	0·0683	0·41	0·51	$2p_5-4d_1$
5401	14·46	148·4	0·0974	0 94	1·65	$1{\cdot}5s_4-2p_1$
5343	13·54	128·3	0·106	0·56	1·06	$2p_{10}-4d_6$
5341	13·54	128·3	0·106	0·56	1·06	$2p_{10}-4d_5$
5331	13·36	124·7	0·107	0·50	0·96	$2p_{10}-4d_3$

* Becoming inaccurate owing to the insensitivity of the plate.

wedge-spectrum. By "ordinary" Neon spectrum is meant the light from a Plücker type of capillary tube of about 1 mm. bore, filled with gas to a pressure corresponding to 1 mm. dark space.

Table II. shows the effect of different types of discharge on the "ordinary" Neon spectrum. By "bulb" discharge is meant the light from the wide bulb part of the tube when a very mild condensed discharge was passed.

TABLE II.

Comparison of Absolute Intensities in Ordinary, Bulb, and Condensed Discharges.

Series.	*n.*	Wave-length.	P.	(*a*).	(*b*).	(*c*).	*b*/*a*.	*c*/*a*.	*c*/*b*.
$1 \cdot 5s_5 - 2p_n$	9	6402	20	100	100	100	1·00	1·00	1·00
	8	6334	10	41·4	58·8	60·9	1·42	1·47	1·04
	7	6217	15	14·5	28·6	32·8	1·97	2·26	1·15
	6	6143	12	34·5	52·9	64·5	1·53	1·87	1·22
	5	5975	12	6·52	19·6	20·4	3·01	3·13	1·04
	4	5945	10	19·2	42·8	44·7	2·23	2·33	1·04
	2	5881	20	12·5	28·5	39·0	2·28	3·12	1·37
$1 \cdot 5s_4 - 2p_n$	8	6506	15	61·4	82·3	87·2	1·34	1·42	1·06
	7	6383	12	47·2	65·6	80·2	1·39	1·70	1·22
	6	6305	6	17·1	35·6	39·0	2·08	2·28	1·09
	4	6096	8	24·1	45·3	55·9	1·88	2·32	1·23
	3	6074	10	19·4	32·4	45·6	1·67	2·35	1·41
	2	6030	10	7·16	17·5	23·8	2·44	3·32	1·36
$1 \cdot 5s_3 - 2p_n$	10	7032	10	127	201	146	1·58	1·15	0·726
	7	6533	6	27·3	48·9	55·7	1·79	2·04	1·14
	5	6266	15	22·6	38·6	50·9	1·71	2·25	1·32
	2	6164	12	14·6	28·3	42·6	1·94	2·92	1·50
$1 \cdot 5s_2 - 2p_n$	6	6929	10	80·9	124	127	1·53	1·57	1·02
	5	6717	2?	45·4	73·5	84·9	1·62	1·87	1·15
	4	6678	9	59·1	86·9	101	1·47	1·71	1·16
	2	6599	15	35·0	57·1	76·3	1·63	2·18	1·34
	1	5852	50	40·9	64·2	65·8	1·57	1·61	1·02
$2p_4 - 3 \cdot 5s_1$	—	5902	6	1·07	4·62	3·79	4·32	3·54	0·820
$2p_8 - 4d$	—	5820	10	1·12	5·00	3·81	4·46	3·40	0·762
$2p_9 - 4d_4$	—	5764	15	1·76	7·76	5·93	4·41	3·37	0·764

P = Intensity according to Paschen.
a = Intensity of ordinary discharge.
b = Intensity of bulb discharge.
c = Intensity of condensed discharge.

It will be noted that the various principal series of any one group diminish in intensity with diminishing wave-length.

The bulb discharge enhances all the principal series, the degree of enhancement in any one group increasing with diminishing wave-length. The same effect is apparent with the condensed discharge, *e.g.* the s_4 and s_3 groups show it without exception. The effect c/b is, however, much less than b/a.

These facts account for the intense yellow colour of the light from Neon tubes excited by the condensed discharge, in contrast with the deep orange colour under normal excitation.

A few lines show anomalous variations, usually in both the condensed and bulb discharges (if at all). λ 5975, which is very weak ordinarily, shows exceptional enhancement under these conditions. The intensity of λ 6143 appears to vary in such a way as to compensate that of its neighbour λ 5975. The line λ 6305 is unduly weak in the condensed discharge, while λ 5852, a yellow line which shows many notable variations—as will be seen later—is enhanced to the average extent by a bulb discharge, but left unchanged by a condensed discharge. There are two diffuse lines and one sharp line (a quartet) recorded under all the conditions of excitation. The effect of a bulb discharge on these is a very strong enhancement,—over fourfold,—and of a different order to that of the principal lines. In further contrast to the latter the condensed discharge then reduces the degree of enhancement. The two diffuse series show almost identical behaviour in this respect, though—as in the case of helium—the effect may only be a reduction of the central intensities, and not of the energy content of the lines, which are probably broadened. The effects of the bulb and condensed discharges would therefore be sufficiently different to distinguish the subsidiary series from the principal series of a spectrum.

Table III. shows the influence of high pressure (25 mm.) on the development. Referred to the usual standard of 100 for λ 6402, most of the lines are enhanced (*vide* b/a column), although a few in the yellow are reduced. The regularity is somewhat broken, but there is a tendency for the less refrangible series of a group to exhibit the greater enhancement (*vide* the $1{\cdot}5s_3-2p_n$ group). This accounts for the deeper orange colour of the high pressure tubes.

Correlating the c/b column of Table III. with the c/a column of Table II., we have a comparison of the behaviour of the condensed discharge under different conditions of pressure. It is true that the intensity of the condensed discharge cannot be reproduced in successive experiments, and that therefore the broadening of the lines may be different and the central intensities alter as a consequence. Indeed, with the 25 mm. tube the condensed discharge was probably milder, and therefore for the same energy content of a line the central intensity should be more pronounced. It will be seen, however, from the respective columns of Tables II. and III., that without exception the enhancement due to the condensed discharge is less at high pressure than at low pressure for the s_5, s_4, and s_3 groups. In the s_2 group the intensities are comparable and show an enhancement in some cases. Possibly this is accounted for by the above facts.

TABLE III.

Influence of Pressure (Absolute Intensities).

Series.	*n*.	Wave-length.	(*a*).	(*b*).	(*c*).	*b*/*a*.	*c*/*a*.	*c*/*b*.
$1{\cdot}5s_5-2p_n$	9	6402	100	100	100	1·000	1·000	1·000
	8	6334	41·4	42·6	50·2	1·029	1·212	1·178
	7	6217	14·5	16·7	25·1	1·152	1·731	1·503
	6	6143	34·5	44·8	52·8	1·229	1·529	1·177
	5	5975	6·52	5·89	17·1	0·903	2·623	2·903
	4	5945	19·2	19·2	35·3	1·000	1·836	1·836
	2	5882	12·5	12·5	30·8	1·000	2·464	2·464
$1{\cdot}5s_4-2p_n$	8	6506	61·4	67·9	85·0	1·106	1·384	1·252
	7	6383	47·2	67·3	71·3	1·426	1·511	1·059
	6	6305	17·1	15·8	26·8	0·924	1·567	1·696
	4	6096	24·1	28·3	41·5	1·174	1·722	1·466
	3	6074	19·4	18·3	34·1	0·943	1·758	1·863
	2	6030	7·16	7·23	18·5	1·010	2·584	2·559
$1{\cdot}5s_3-2p_n$	10	7032	127	270	241	2·126	1·898	0·893
	7	6533	27·3	36·3	53·5	1·330	1·960	1·474
	5	6266	22·6	29·4	40·9	1·301	1·810	1·391
	2	6163	14·6	16·3	23·3	1·116	1·596	1·429
$1{\cdot}5s_2-2p_n$	6	6929	80·9	93·4	177	1·154	2·188	1·895
	5	6717	45·4	58·6	114	1·291	2·511	1·945
	4	6678	59·1	75·7	134	1·281	2·267	1·770
	2	6599	35·0	44·8	93·2	1·280	2·663	2·080
	1	5852	40·9	19·3	55·1	0·472	1·347	2·855
$2p_4-3{\cdot}5s_1$	—	5902	1·07	—	—	—	—	—
$2p_8-4d_4$	—	5820	1·12	—	—	—	—	—
$2p_9-4d_4$	—	5764	1·76	—	—	—	—	—

a=Capillary tube—Ordinary uncondensed discharge.
b=Capillary tube—Uncondensed discharge—25 mm. pressure.
c=Capillary tube—Mild condensed discharge—25 mm. pressure.

As before, λ 5975 is a line of exceptional variation, being reduced in intensity at high pressure, but showing exceptional enhancement in the condensed discharge. The compensating behaviour of λ 6143 is again apparent. λλ 6305, 6074 show a slight reduction in high pressure, which, however, is obscured by the condensed discharge. λ 5852 again shows large variations, being reduced to 0·472 of its value by high pressure. The condensed discharge, although enhancing it by the large factor 2·85, leaves it still of exceptionally low intensity as compared with its neighbours in the group. It will be seen later that λ 5852 is essentially a "low pressure" line. As at "ordinary" pressure, so at high pressure the condensed discharge displaces the energy towards the more refrangible principal series of a group.

The lines λ 5902 (sharp), and λλ 5820 and 5764 (diffuse) do not appear at high pressure, *even on some comparatively strong plates* (either with uncondensed or condensed discharges). Though it would be unwise to generalize on so small a basis, it is possible, therefore, that high pressure tends to throw the energy into the principal series at the expense of the subsidiary series.

From the b/a column of Table IV. it is clear that the effect of low current density (such as would obtain in a tube of 15 mm. bore compared with a capillary bore of 1 mm.) is to displace the energy to the less refrangible principal series of any group. With slight irregularities this is noticeable in the s_5, s_4, and s_3 groups, and it is the reason for the pronounced red colour of pure Neon in wide bore discharge tubes. The effect apparently reverses in the s_2 group, the reversal being similar to that previously recorded in connexion with Table III., in which the displacement of energy to the more refrangible side by the condensed discharge was compared at different pressures.

The general effect of very low pressure (*vide* column c/b) is to displace the energy towards the more refrangible series in any group: the opposite effect of very high pressure.

The lines λλ 6143, 5975, as before, show anomalous variations under low current density, the former being reduced by comparatively little, and the latter by too much, while low pressure has no notable effect. λ 5852 is tremendously reduced in intensity by low current density, and equally notably enhanced at very low pressure. Under the latter condition it becomes the dominating line in the spectrum, much as the green line λ 5015 of helium behaves under similar circumstances. It is perhaps noteworthy that λ 5015 is a member of the principal series of singlets of helium.

The two diffuse lines λλ 5820, 5764, of which we saw no sign under conditions of high pressure (*vide* Table IV.), are notably enhanced at very low pressure—viz., by the factors 6·88, 5·35. The sharp line λ 5902 does not appear.

The low pressure photograph gave the following three lines of helium and two of hydrogen with the approximate intensities indicated:—λλ 5015, (51); 4713, (15); 4471, (13); 6563, (65); 4861, (11). These gases could only have been present, however, in *very* small proportions.

TABLE IV.

Effect of Very Low Pressure and Current Density.

Series.	*n*.	Wave-length.	(*a*).	(*b*)*.	(*c*).	*b*/*a*.	*c*/*a*.	*c*/*b*.
$1·5s_5-2p_n$	9	6402	100	100	100	1·000	1·000	1·000
	8	6334	41·4	24·9	52·4	0·601	1·266	2·104
	7	6217	14·5	5·13	14·0	0·354	0·966	2·729
	6	6143	34·5	23·9	51·6	0·693	1·496	2·159
	5	5975	6·52	-	9·46	—	1·451	—
	4	5945	19·2	6·66	27·9	0·347	1·453	4·189
	2	5882	12·5	4·96	26·2	0·397	2·096	5·282
$1·5s_4-2p_n$	8	6506	61·4	75·4	121	1·228	1·971	1·605
	7	6383	47·2	44·8	62·6	0·949	1·345	1·397
	6	6305	17·1	6·35	17·2	0·371	1·006	2·709
	4	6096	24·1	9·99	43·1	0·415	1·788	4·314
	3	6074	19·4	6·73	32·2	0·347	1·660	4·785
	2	6030	7·16	2·60	10·2	0·363	1·425	3·923
$1·5s_3-2p_n$	10	7032	127	235	—	1·850	—	—
	7	6533	27·3	22·1	29·3	0·810	1·073	1·326
	5	6266	22·6	10·9	28·3	0·482	1·252	2·596
	2	6163	14·6	5·31	19·4	0·364	1·329	3·653
$1·5s_2-2p_n$	6	6929	80·9	56·3	156	0·696	1·928	2·771
	5	6717	45·4	28·1	82·6	0·619	1·819	2·940
	4	6678	59·1	40·6	136	0·687	2·301	3·350
	2	6599	35·0	24·8	63·4	0·709	1·811	2·556
	1	5852	40·9	4·41	173	0·108	4·230	39·23
$2p_4-3·5s_1$	—	5902	1·07	—	—	—	—	—
$2p_8-4d_4$	—	5820	1·12	—	6·86	—	6·13	—
$2p_9-4d_4$	—	5764	1·76	—	8·25	—	4·69	—

a = Capillary tube—Ordinary discharge—about 1 mm. pressure.
b = Wide bore tube—25 mm. pressure.
c = Wide bore tube—Very low pressure.

---

* This tube unfortunately contained a trace of carbon, which may have superposed a specific effect on that due to high pressure Neon in a wide bore tube.

TABLE V.

Effect of Admixture of Hydrogen.

Series.	*n.*	Wave-length.	(*a*).	(*b*).	(*c*).	*b*/*a*.	*c*/*a*.	*c*/*b*.
$1{\cdot}5s_5-2p_n$	9	6402	100	100	100	1·000	1·000	1·000
	8	6334	41·4	43·3	26·2	1·046	0·634	0·606
	7	6217	14·5	13 6	5·21	0·938	0·359	0·383
	6	6143	34·5	35·0	40 8	1·014	1·181	1·165
	5	5975	6·52	6·26	4·45	0·960	0·683	0·711
	4	5945	19·2	19·5	17·2	1·016	0·897	0·883
	2	5882	12·5	11·4	10·7	0·912	0·855	0·938
$1{\cdot}5s_4-2p_n$	10	7245	84·3	57·9	—	0·687	—	—
	8	6506	61·4	59 3	61·5	0·966	1·001	1·037
	7	6383	47·2	49·8	35·5	1·055	0·752	0·712
	6	6305	17·1	17·9	9·13	1·047	0·534	0·510
	4	6096	24·1	23·2	25·4	0·963	1·052	1·093
	3	6074	19·4	19·5	17·0	1·007	0·877	0·871
	2	6030	7·16	7·06	5·12	0·986	0·715	0·725
	1	5400	1·65	0·72	—	0·436	—	—
$1{\cdot}5s_3-2p_n$	10	7032	127	93·8	—	0·737	—	—
	7	6533	27·3	26·7	23·4	0·987	0·858	0·878
	5	6266	22·6	24·3	18·6	1·075	0·823	0·766
	2	6163	14·6	16·0	11·0	1·096	0·755	0·689
$1{\cdot}5s_2-2p_n$	6	6929	80·9	60·5	66·8	0·748	0·825	1·104
	5	6717	45·4	36·5	32·6	0·804	0·719	0·894
	4	6678	59·1	49·5	57·0	0·838	0·965	1·152
	2	6599	35·0	29·5	31·9	0·843	0·911	1·081
	1	5852	40·9	38·3	126	0·936	3·076	3·285
$2p_9-3{\cdot}5s_5$	—	6182	0·79	0·68	—	0·861	—	—
$2p_4-3{\cdot}5s_1$	—	5902	1·07	1·21	—	1·131	—	—
$2p_6-4d_4$	—	5991	0·45	0·42	—	0·933	—	—
$2p_6-4d_3$	—	5988						
$2p_8-4d_4$	—	5820	1·12	1·09	—	0·973	—	—
$2p_9-4d_4$	—	5764	1·76	1·62	—	0·920	—	—
$2p_{10}-4d_6$	—	5343	1·06	0·88	—	0·830	—	—
$2p_{10}-4d_5$	—	5341						
$2p_{10}-4d_3$	—	5330	0·96	0·73	—	0·760	—	—
H_α	—	6562	—	1·37	691	—	—	504
H_β	—	4861	—	—	236	—	—	—
H_γ	—	4340	—	—	65·6	—	—	—
H_δ	—	4102	—	—	7·53	—	—	—

a = Pure Neon.
b = Neon with a trace of hydrogen.
c = Neon with a quantity of hydrogen.

The data of Table V. were obtained by admitting hydrogen through a palladium regulator into the Plücker tube containing "ordinary" low pressure Neon. The admixture of a trace of hydrogen produces comparatively little alteration.

It is probably true to say that within the limits of experimental error the effect is negligible on the s_5 and s_4 groups, with a tendency to displace the energy to the more refrangible series in the s_3 and s_2 groups. A quantity of hydrogen affects a general reduction of intensity, but there is no apparent regularity. The c/b and c/a columns show that the reduction is different for the different lines. The greater part of the light emission in case (*c*) arises from the Balmer Series: the photographic intensities of the recorded Neon lines were all comparatively small. The behaviour of λ 5852 is again notable. A quantity of hydrogen affects a threefold enhancement of this line, in striking contrast to the other lines of Neon.

Column (*b*) of Table VI. exhibits some noteworthy changes. The very considerable intensity reduction of all the lines is at once apparent. This accords naturally with the fact that they disappear completely for greater proportions of argon. The reduction, however, is not uniform, but exhibits a pronounced intensity displacement towards the red end in each group. This of course may be due either to the high pressure together with the low current density consequent upon using a wide bore tube, or to the specific action of argon, or to both of these causes. A comparison with the b/a column of Table IV. (which is reproduced in Table VI.) shows that with the possible exception of the s_2 group the former cause accounts for the whole of this. Column c/a shows, with some fluctuations, an energy displacement towards the shorter wave-lengths. There are, however, five factors concerned in this intensity distribution: mild condensed discharge conditions, low current density, high pressure of gas, the presence of a little hydrogen, and the presence of a trace of argon. We proceed to attach weight to these in comparison with results already obtained.

Comparison with the b/a and c/a columns of Table II. shows a satisfactory correspondence throughout the s_5 and s_4 groups, the intensities in question being intermediate between these values. In the s_3 and s_2 groups the discharge conditions cannot account wholly for the intensities, which are in general greater than those of Table II. Consider now the c/a column of Table III., which includes the same conditions of discharge and pressure. Compared with these the intensities of Table VI. (column c/a) are uniformly greater and show, particularly in the s_3 and s_2 groups, evidence of an additional energy displacement to the shorter wave-lengths. The effect of low current density (*vide* the b'/a column) is the reverse of this. There remain the effects of hydrogen and argon

TABLE VI.

Trace of Argon in 25 mm. Neon (wide bore).

Series.	*n*.	Wave-length.	(*a*).	(*b*).	(*c*).	*b′*/*a*.	*b*/*a*.	*c*/*a*.
$1{\cdot}5s_5-2p_n$	9	6402	100	100	100	1·000	1·000	1·000
	8	6334	41·4	20·0	56·4	0·601	0·483	1·362
	7	6217	14·5	—	29·1	0·354	—	2·008
	6	6143	34·5	17·2	59·4	0·693	0·497	1·722
	5	5975	6·52	—	20·3	—	—	3·117
	4	5945	19·2	5·32	45·1	0·347	0·277	2·349
	2	5882	12·5	—	32·6	0·397	—	2·608
$1{\cdot}5s_4-2p_n$	10	7245	84·3	—	185	—	—	2·190
	8	6506	61·4	38·8	84·8	1·228	0·632	1·381
	7	6383	47·2	34·5	77·6	0·949	0·731	1·645
	6	6305	17·1	—	30·9	0·371	—	1·806
	5	6128	—	—	9·70	—	—	—
	4	6096	24·1	8·60	47·2	0·415	0·357	1·957
	3	6074	19·4	5·82	38·2	0·347	0·300	1·971
	2	6030	7·16	—	21·4	0·363	—	2·983
	1	5400	1·65	—	5·43	—	—	3·291
$1{\cdot}5s_3-2p_n$	10	7032	127	—	254	1·850	—	1·998
	7	6533	27·3	18·9	66·9	0·810	0·693	2·449
	5	6266	22·6	9·63	50·9	0·482	0·426	2·253
	2	6163	14·6	4·12	36·7	0·364	0·282	2·514
$1{\cdot}5s_2-2p_n$	6	6929	80·9	—	162	0·696	—	2·000
	5	6717	45·4	—	115	0·619	—	2·524
	4	6678	59·1	49·0	138	0·687	0·829	2·333
	2	6599	35·0	22·1	88·6	0·709	0·630	2·530
	1	5852	40·9	—	94·2	0·108	—	2·304
$2p_9-3{\cdot}5s_5$	—	6182	0·79	—	2·25	—	—	2·848
$2p_4-3{\cdot}5s_1$	—	5902	1·07	—	5·14	—	—	4·804
$2p_6-4d_4$	—	5991	0·45	—	2·41	—	—	5·356
$2p_6-4d_3$	—	5988						
$2p_5-4d_4$	—	5820	1·12	—	5·01	—	—	4·473
$2p_5-4d_1$	—	5804	0·48	—	1·97	—	—	4·104
$2p_9-4d_4$	—	5764	1·76	—	8·39	—	—	4·767
$2p_9-4d_1$	—	5748	0·51	—	2·33	—	—	4·569
$2p_9-5d_4$	—	5037	—	—	3·16	—	—	—
$2p_{10}-4d_6$	—	5343	1·06	—	5·98	—	—	5·642
$2p_{10}-4d_5$	—	5341						
$2p_{10}-4d_3$	—	5331	0·96	—	5·36	—	—	5·583
$2p_{10}-5d_6$	—	4710	—	—	0·97	—	—	—
$2p_{10}-5d_5$	—	4709						
$2p_{10}-5d_3$	—	4704	—	—	0·93	—	—	—

a = Pure Neon—Capillary tube—Ordinary discharge.

b = Trace of argon in 25 mm. Neon—Wide bore tube—Uncondensed discharge.

c = „ „ „ Mild condensed discharge.

b′ = Pure Neon · Wide bore tube—25 mm. pressure (Table IV.).

admixture to account for the observed values. Taking the case of the s_3 group, which is critical, Table V. shows us that while a trace of hydrogen ($H_\alpha = 1{\cdot}37$) gives an intensity displacement to the shorter wave-lengths, a large quantity ($H_\alpha = 691$) reverses this. It is a matter of opinion which of these extremes the present case ($H_\alpha = 12{\cdot}95$) resembles the more closely, and upon the discrimination depends the estimation of the effect of a trace of argon. It is clear that much more extensive and accurate work will be required to differentiate between the various effects.

It is perhaps worth mentioning that under the conditions of column (*b*) no argon lines appeared, but with the mild condensed discharge of column (*c*) most of the strongest lines of "red" argon were recorded, together with $H_\alpha(12{\cdot}95)$, $H_\beta(5{\cdot}02)$, $H_\gamma(2{\cdot}04)$.

Table VII. records the intensities of Neon lines radiated from a trace of Neon mixed with 25 mm. of helium in a wide bore tube. The light of the uncondensed discharge is a soft red colour, the greater part being due to Neon, although the strongest helium lines are visible. A mild condensed discharge yields a very intense yellow light, a very large number of sharp and diffuse lines of Neon now being radiated, together with the complete arc spectrum of helium (strongly) and a few of the helium bands. In the former case H_α has a strength of 1·7, in the latter case of 320. It was felt that it would serve no useful purpose at present to give under the respective columns of Table VII. a complete record of these lines. The record has therefore been limited to those lines which have been recorded in previous tables. The intensities of lines in the extreme red, such as λλ 7245 and 7032 are of course subject to considerable errors owing to the comparative insensitivity of the photographic plate in that neighbourhood. No useful purpose would seem to be served at present by discussing the detail of Table VII., as there are numerous exceptions to any rules that can be framed. There seems to be a tendency to displacement of the energy to the shorter wave-lengths. Among the lines of exceptional variation are λλ 6217, 6074, 5975, and 5852.

The recorded results, however, indicate very considerable intensity variations, particularly with the sharp and diffuse lines. This is of quite a different order to the effect on the principal lines; and it should, for example, be possible to apply this test of the degree of enhancement in the presence of high pressure helium to separate a complex spectrum into principal and subsidiary lines.

TABLE VII.

Trace of Neon in 25 mm. Helium.

Series.	*n*.	Wave-length.	(*a*).	(*b*).	(*c*).	*b*/*a*.	*c*/*a*.
$1·5s_5-2p_n$	9	6402	100	100	100	1·000	1·000
	8	6334	41·4	50·7	48·1	1·225	1·162
	7	6217	14·5	26·1	27·6	1·800	1·903
	6	6143	34·5	49·2	43·0	1·426	1·246
	5	5975	6·52	15·0	29·6	2·301	4·540
	4	5945	19·2	24·1	26·4	1·255	1·375
	2	5882	12·5	43·4*	433*	3·472	34·64
$1·5s_4-2p_n$	10	7245	84·3	345	320	4·093	3·796
	8	6506	61·4	112	95·9	1·824	1·562
	7	6383	47·2	100	91·2	2·119	1·932
	6	6305	17·1	38·4	37·7	2·246	2·205
	5	6128	—	—	—	—	—
	4	6096	24·1	48·0	42·1	1·992	1·747
	3	6074	19·4	33·7	27·2	1·737	1·402
	2	6030	7·16	18·6	19·7	2·598	2·751
	1	5400	1·65	1·28	4·35	0·776	2·636
$1·5s_3-2p_n$	10	7032	127	380	411	2·992	3·236
	7	6533	27·3	39·3	74·3	1·440	2·722
	5	6266	22·6	39·2	41·5	1·735	1·836
	2	6163	14·6	41·1	37·7	2·815	2·582
$1·5s_2-2p_n$	6	6929	80·9	145	225	1·792	2·781
	5	6717	45·4	85·3	134	1·879	2·952
	4	6678	59·1	110	432†	1·861	7·310
	2	6599	35·0	88·5	109	2·529	3·114
	1	5852	40·9	50·2	108	1·227	2·641
$2p_9-3·5s_5$	—	6182	0·79	13·2	18·8	13·71	23·80
$2p_4-3·5s_1$	—	5902	1·07	4·75	24·7	4·439	23·08
$2p_8-4d_4$	—	5991	0·45	3·46	9·89	7·689	21·98
$2p_6-4d_3$	—	5988					
$2p_5-4d_4$	—	5820	1·12	9·72	27·1	8·679	24·20
$2p_9-4d_4$	—	5764	1·76	17·0	53·4	9·660	30·34
$2p_{10}-4d_6$	—	5343	1·06	10·7	30·2	10·09	28·49
$2p_{10}-4d_5$	—	5341					
$2p_{10}-4d_3$	—	5330	0·96	8·63	26·7	8·990	27·81

a=Pure Neon—Capillary tube—Ordinary discharge.
b=Trace of Neon in 25 mm. helium—Uncondensed discharge.
c= ,, ,, ,, Mild condensed discharge.

* Helium line λ 5875 superposed.
† ,, λ 6678 ,,

It is perhaps appropriate to mention here that a noticeable intensity change induced by helium in a Neon doublet λλ 743·78, 735·95 has been recorded by Lyman and Saunders‡.

---

‡ 'Nature,' vol. cxvi. p. 358 (1925).

Ordinarily the more refrangible component is the stronger, whereas the reverse is true when the pair are developed in high pressure helium.

TABLE VIII.

Effect of admixture of CO_2.

Series.	*n.*	Wave-length.	(*a*).	(*b*).	(*c*).	*b*/*a*.	*c*/*a*.
$1{\cdot}5s_5-2p_n$	9	6402	100	100	100	1·000	1·000
	8	6334	42·6	46·8	38·0	1·098	0·892
	7	6217	16·7	15·7	9·56	0·941	0·572
	6	6143	44·8	35·7	46·4	0·797	1·036
	5	5975	5·89	5·73	7·59	0·973	1·289
	4	5945	19·2	17·0	24·5	0·887	1·276
	2	5882	12·5	10·4	13·3	0·833	1·062
$1{\cdot}5s_4-2p_n$	10	7245	—	16·4	—	—	—
	8	6506	67·9	77·0	101	1·134	1·493
	7	6383	67·3	59·9	73·5	0·890	1·092
	6	6305	15·8	17·9	15·6	1·133	0·984
	5	6128	—	—	—	—	—
	4	6096	28·3	21·1	36·1	0·747	1·277
	3	6074	18·3	16·1	23·2	0·880	1·268
	2	6030	7·23	6·77	7·78	0·937	1·076
	1	5400	—	—	6·95	—	—
$1{\cdot}5s_3-2p_n$	10	7032	270	258	237	0·956	0·878
	7	6533	36·3	46·4	37·9	1·278	1·043
	5	6266	29·4	26·5	32·5	0·901	1·105
	2	6163	16·3	15·4	17·1	0·942	1·051
$1{\cdot}5s_2-2p_n$	6	6929	93·4	110	168	1·175	1·799
	5	6717	58·6	65·2	95·2	1·113	1·624
	4	6678	75·7	81·8	145	1·081	1·917
	2	6599	44·8	48·7	68·9	1·087	1·538
	1	5852	19·3	22·0	193	1·140	10·00
$2p_4-3{\cdot}5s_1$	—	5902	—	0·40	3·25	—	—
$2p_8-4d_4$	—	5820	—	—	3·67	—	—
$2p_9-4d_4$	—	5764	—	0·59	5·31	—	—

a=Pure Neon—Capillary tube, 25 mm. pressure—Uncondensed discharge. (Table III. (*b*).)
b=High pressure Neon and CO_2—Capillary tube.
c= „ „ „ Cathode glow.

The data of Table VIII. were obtained from a tube consisting of a bulb having a large flat cathode in it, while a capillary portion was joined on to this bulb. The tube was filled with Neon to a pressure of about 25 mm. and possessed a side bulb of magnesite, by means of which CO_2 could be admitted as desired. The admission of the latter to a pressure of some mm. caused the cathode glow to contract to a thin bright yellow layer about 1 mm. in breadth. The results of an "end-on" photograph of this are given in column (*c*), while column (*b*) gives the light from the capillary under these conditions. The outstanding feature of the spectrum of the cathode glow is the line λ 5852, which has a ten-fold enhancement, and gives the glow its characteristic bright yellow colour.

TABLE IX.

Intensities at various distances from the Cathode.

Series.	*n*.	Wave-length.	0 mm.	1 mm.	2 mm.	3 mm.	4 mm.	5 mm.
$1{\cdot}5s_5-2p_n$	9	6402	100	108	113	121	114	82·0
	8	6334	23·0	24·6	34·4	39·8	25·6	20·4
	6	6143	35·1	36·7	52·0	54·9	38·3	31·2
	4	5945	18·2	16·7	24·8	23·0	16·6	12·4
	2	5882	11·9	10·3	12·9	15·5	12·4	5·09*
$1{\cdot}5s_4-2p_n$	8	6506	57·0	64·6	91·8	102	71·1	53·9
	7	6383	31·1	27·9	40·9	45·7	29·5	22·3
	5	6305	8·20	4·64*	10·8	11·2	4·64*	4·64*
	4	6096	23·4	21·3	35·8	36·7	26·6	18·6
	3	6074	16·5	14·9	21·6	21·8	15·3	12·2
$1{\cdot}5s_3-2p_n$	10	7032	199	227	284	316	258	137*
	5	6266	16·5	18·7	26·2	26·8	18·3	13·8
	2	6163	9·35	11·4	14·8	14·5	10·6	7·17
$1{\cdot}5s_2-2p_n$	6	6929	205	240	318	406	257	190
	5	6717	46·2	50·4	77·1	83·9	54·2	41·3
	4	6678	76·8	104	108	104	78·1	73·3
	2	6599	17·7	22·2	24·6	28·6	22·0	10·8*
	1	5852	86·9	101	164	184	112	67·0

* These lines were not visible. The values tabulated are absolute intensities corresponding to a photographic intensity =1 in each case (*i. e.* just visible).

We have also made a study of the distribution of intensity in the spectrum of neon, as a function of the distance from a flat cathode, similar to work done by Merton and Nicholson (*loc. cit.*). The pressure of gas was such as to give a dark space of about 1 mm. The curves representing the intensity of emission as a function of distance are somewhat similar for the various lines, though the amplitude variations of the curves differ. In most cases the maximum intensity of emission was about 2·5 mm. from the cathode. We have not thought it desirable to enter into a fuller discussion of these results until similar information for a number of sharp and diffuse lines is available.

November 27th, 1925.

DESCRIPTION OF PLATE.

1. Positive crater of the carbon arc with "ordinary" Neon spectrum in juxtaposition.
2. Mild condensed discharge through a trace of Neon in high pressure helium. Wide bore tube. (*Vide* Table VII.)

3*a*. Uncondensed discharge through a trace of Neon in high pressure helium. Wide bore tube. (*Vide* Table VII.)
3*b*. "Ordinary" Neon spectrum. Plücker tube. Capillary bore. Pressure corresponding to about 1 mm. dark space.
4*a*. Ordinary spectrum of pure Neon as above. (*Vide* Table V.)
4*b*. Same as above plus a trace of hydrogen.
4*c*. Same as above plus a quantity of hydrogen (say 2 or 3 mm.).
5*a*. Ordinary spectrum of pure Neon as above. (*Vide* Table IV.)
5*b*. Neon at 25 mm. pressure in wide bore tube.
5*c*. Neon at very low pressure in wide bore tube. (Fluorescence of glass visible: say about 1/100 mm.)

LIII. *Note on the Structure of Cadmium and Zinc Resonance Lines.* *By* Prof. R. W. Wood *.

[Plate XI.]

THE structure of the 2536 line of mercury was reported in this Journal (vol. i. p 762, 1925), but the other, resonance line 1849 has not yet been examined. A possible method might be to use an echelon by reflexion, mounting the entire apparatus *in vacuo*. I have examined the mercury green line in this way, and found the resolution of the companion lines fairly good. Since the publication of the paper referred to above I have examined the fine structure of the $1S-2p_2$ and $1S-2P$, the analogous lines of cadmium and zinc.

The source of light in each case was a metallic arc in a tube of fused quartz furnished with an anode of tungsten wire. The tube was continuously exhausted by a mercury-vapour pump during its operation, and the cathode bulb, which contained the metal, was immersed in water.

The fine structure of the lines was photographed with the two quartz Lummer-Gehrcke plates described in the earlier paper, but in this case the plates were employed in succession, and not crossed. The structure of the 2536 Hg-line, as was shown in the earlier paper, is less complicated than the structure figured by Nagaoka, whose photographs were complicated by absorption. It consists of five lines of nearly equal intensity and almost equidistant. The corresponding lines of cadmium and zinc showed a much simpler structure, as was to be expected.

---

* Communicated by the Author.

The fringes formed by the interference plates were focussed on the slit of a small quartz spectrograph by means of a quartz-fluorite objective of 40 cm. focus. The structure of the cadmium lines obtained in this way is shown on Plate XI., the photographs being reproduced as negatives. Figs. 1 and 2 show the 2288 line obtained with the thin and thick Lummer plates respectively. The constants of the two plates will be found in the paper following the present note. It was at first thought that the line might be single, but strongly reversed. This, however, is not the case, as the appearance is the same with the discharge pressed against the front and back wall of the tube by a magnetic field. In the latter case the absorption is very strong, but the lines are merely weakened as a whole, with no trace of reversal down the centre, as was the case with the five components of Hg 2536. The wave-length separation of the lines was computed by Dr. McNair, who extended the work to the other lines of the spectrum. The values found were ·000 and ·021 (or $-$·017). In the case of 3261, which is analogous to Hg 2536 ($1S-2p_2$), we have a strong and easily reversed line accompanied by a faint companion on the short wave-length side: separation ·000 and $-$·019. Figs. 3 and 5 show the line as given by the thin and thick plates, and fig. 5 shows the main line so strongly reversed (by driving the discharge against the back wall) that the components of the reversed line are not much more intense than the faint companion. In the case of zinc 2138·6 $1S-2P$ was found to be double, like Cd 2288, while 3075·9 $1S-2p_2$ was single.

LIV. *The Fine Structure of Certain Lines and Energy Levels of Cadmium.* *By* WALTER A. MACNAIR, *National Research Fellow* *.

[Plate XII.]

PART I.

RECENT attempts have been made to obtain the fine structure of the energy levels of certain elements from the fine structure of their spectrum lines by Ruark, Mohler and Chenault †, by Ruark and Chenault ‡, and by Joos §. It is evident that if anything like a complete fine structure energy level diagram of any one element is to be constructed the fine structure of many lines of that element must be obtained. The work reported here is the beginning of an attempt to obtain the fine structure of the spectrum lines of the elements in the zinc-cadmium group, and also the structure of their energy levels.

The light from a cadmium arc was passed through a crystalline quartz lens screened by a vertical slit about a centimetre wide and ten centimetres long. At the focus of the lens the light was passed through a small quartz double-image prism and then into a quartz Lummer-Gehrcke plate. The fringe systems of all of the spectrum lines were focussed simultaneously (using the beam polarized with the electric vector parallel to the parallel surfaces of the Lummer-Gehrcke plate) by a quartz-fluorite achromatic lens on the slit of a spectrograph, so that a plate exposed in the spectrograph gave the fine structure of all of the lines at once. Two different quartz spectrographs and two different grating spectrographs were used at various times during the investigation. The technique of using Lummer-Gehrcke plates in the ultra-violet region has been described by Professor Wood in the Philosophical Magazine ||.

The cadmium arc was made of quartz tubing of 8 mm. inside diameter. The tungsten-wire anode was sealed in at one end by means of hard glass and intermediate glasses, and the metallic cadmium cathode, which was about 15 centimetres from the end of the tungsten wire, was kept cool by dipping the cathode end of the arc in running

---

* Communicated by Prof. R. W. Wood.

† 'Nature,' cxiv. p. 575 (1924).

‡ Phil. Mag. l. p. 937 (1925).

§ *Phys. Zeits.* xxvi. No. 10 (1925).

|| Wood, R. W., Phil. Mag. l. pp. 762-763 (1925).

water. The light from the side of the arc several centimetres from the cathode was observed.

Two quartz Lummer-Gehrcke plates made by Adam Hilger & Co. were used. One is 4·40 mm. thick and 130 mm. long, and the other is 6·55 mm. thick and 200 mm. long. From these dimensions and the optical constants of quartz the distance in A.U. between orders of the fringe system due to a plate can be calculated, as shown by Nagaoka[*] and by Simeon[‡]. The following table gives the values calculated for various wave-lengths :—

TABLE I.

Wave length.	A.U. between consecutive orders.	
	4·40 mm. plate.	6·55 mm. plate.
2000 A.U.	·028	·019
2500 "	·049	·033
3000 "	·076	·051
3500 "	·109	·073
4000 "	·145	·097
4500 "	·186	·125
5000 "	·230	·154
5500 "	·282	·189
6000 "	·341	·229

By comparing three photographs of the fine structure—one taken when a magnetic field forced the arc discharge against the side of the tube nearest the analysing apparatus, another when the discharge was against the opposite side, and the third when no magnetic field was used—it is seen that the main component of each of the following subordinate series lines is reversed under the last two conditions: 5085·9, 3080·9, 3610·5, 3403·6 (the reversal being more complete when the discharge is against the far side of the tube). The other components of these lines and all the components of the other lines observed did not reverse. Professor Wood has reported the behaviour of the resonance lines elsewhere in this journal.

The position of the fringes of each line was determined to ·01 mm. by observing the plates on a dividing engine. Usually the position of the fringes in about ten consecutive orders was recorded. The method of computing the separation of two components in A.U. can be explained by referring to fig. 1.

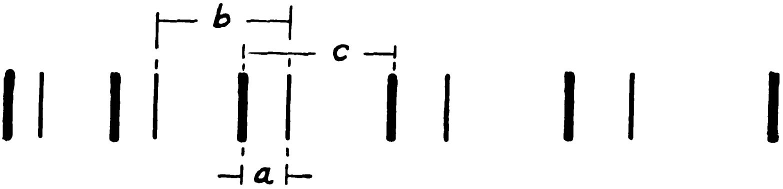
---

[*] Proc. Tokyo Math.-Phys. Soc. viii. (Ser. 2) p. 296.

[†] Journ. Scientific Inst. i. No. 10 (July 1924).

The average of the distances b and c is taken as the separation of orders, in millimetres. Then $\frac{a}{\frac{b+c}{2}}$ times the separation of orders in A.U., as taken from the curves drawn from Table I., gives the separation of components in A.U. The weaker component in fig. 1 is of shorter wave-length than the main component if the pair of components separated by a millimetres is taken as a complete order, as is assumed to be the case in the above illustration. That is, the shorter wave-length components appear on that side of the main component toward which the separation of orders (in millimetres) increases. In deciding to which main component any particular satellite belongs, no ambiguity remains after comparing the interference patterns due to both Lummer-Gehrcke plates, as will be seen by inspecting the reproductions (fig. 2, Pl. XII.) and remembering that the thicker plate has about one and one-half times the dispersion of the thinner one. This simple method is possible when dealing with elements like cadmium, the lines of which have a fine structure which is not spread over such a range as to intermix the orders due to the interferometer so badly that they cannot be easily separated. In but two cases of all with which we are here concerned have the components of two different orders overlapped; these will be pointed out in some remarks on the reproductions.

Fig. 1.



There has been some recent discussion by E. Gehrcke * and P. H. Van Cittert † as to the accuracy and reliability of results obtained with Lummer-Gehrcke plates. G. Hansen ‡ has also discussed the question. Since cadmium is much

---

* *Ann. d. Phys.* lxxviii. p. 461 (1925).

† *Ibid.* lxxvii. p. 372 (1925); lxxix. p. 94 (1926).

‡ *Ibid.* lxxviii. p. 558 (1925).

heavier than hydrogen, the Lummer-Gehrcke plate fringes were naturally much narrower for the former element, which eliminated part of the difficulties Hansen had to contend with. The accuracy of the work reported here may be judged by inspecting Table II., where the observations of the fine structure of three lines by four independent observers may be compared. The greatest difference in the observed positions of any one component is ·001 A.U. Also by inspecting Table III., where the fine structure computed from the measurements on the fringe system due to each plate is reported separately. Here the greatest difference in the computed positions of any one component is ·002 A.U., so that the final results reported are probably correct to ·001 A.U. In four cases the thin plate did not resolve a close satellite sufficiently to allow a reliable measurement. In these cases the results for the thick plate alone are reported.

TABLE II.

Fine Structure of the 5085·9, 4799·9, and 4678·2 Lines of Cadmium.

5085·9 $2p_1-2s$.

+·076 ($\frac{1}{8}$);	·000 (1);	−·026 ($\frac{1}{8}$?)	Janitzki[1].
+·076 (2);	·000 (10);	−·026 (1)	Wali-Mohammad[2].
+·077 (2);	·000 (10);	−·025 (2)	Takamine[3].
+·077 (7);	·000 (10);	−·025 (4)	MacNair.

4799·9 $2p_2-2s$.

+·058 ($\frac{1}{4}$);	·000 (1);	−·034 ($\frac{1}{4}$);	·081 ($\frac{1}{8}$)	Janitzki.
+·058 (6);	·000 (10);	−·034 (3);	·081 (6)	Wali-Mohammad.
+·059 (3);	·000 (10);	−·033 (1);	·080 (2)	Takamine.
+·058 (6);	·000 (10);	−·034 (3);	·081 (3)	MacNair.

4678·2 $2p_3-2s$.

+·030 ($\frac{1}{3}$);	·000 (1);	−·056 ($\frac{1}{6}$)	Janitzki.
+·031 (3);	·000 (10);	−·056 (6)	Wali-Mohammad.
+·031 (4);	·000 (10);	−·057 (2)	Takamine.
+·031 (8);	·000 (10);	−·056 (4)	MacNair.

[1] Janitzka, *Ann. d. Phys.* xix. p. 36 (1906); xxix. p. 833 (1909).

[2] Wali-Mohammad, *Ann. d. Phys.* xxxix. p. 225 (1912).

[3] Takamine, Proc. Tokyo Math.-Phys. Soc. viii. p. 51 (1915).

TABLE III.

Fine Structure of Cadmium Lines. (MacNair.)

[In this Table the main component ·000 (10) has been omitted in each line.]

Line 3252·5:	$2p_1-3s$.	
Thick Plate	+·031;	−·010
Thin Plate	+·031;	——
$\Delta\lambda$ (Intensity)...	+·031 (2);	−·010 (3)
$\Delta\nu$ (cm.$^{-1}$)	−·293;	+·095

Line 3133·2 : $2p_2$–$3s$.
+·024 ; −·012 ; −·032
+·025 ; —— ; −·033
+·024 (1) ; −·012 (1) ; −·033 (1)
−·245 ; +·122 ; +·337

Line 3080·9 : $2p_3$–$3s$.
+·012 ; −·024
+·013 ; −·022
+·013 (3) ; −·023 (2)
−·137 ; +·242

Line 3614·4 : $2p_1$–$3d''$.
+·037 ; −·023
+·038 ; −·023
+·037 (2) ; −·023 (4)
−·283 ; +·176

Line 3610·5 : $2p_1$–$3d$.
−·035
−·037
−·036 (3)
+·276

Line 3466·2 : $2p_2$–$3d'$.
+·031 ; −·016
+·031 ; −·015
+·031 (3) ; −·015 (5)
−·258 ; +·125

Line 3403·6 : $2p_3$–$3d''$.
+·017
+·017
+·017 (5)
−·147

Line 2980·6 : $2p_1$–$4d$.
−·025
−·027
−·026 (1)
+·293

Line 2881·2 : $2p_2$–$4d''$.
+·021 ; −·011
+·022 ; −·010
+·021 (1) ; −·010 (5)
−·253 ; +·120

Line 2836·9 : $2p_3$–$4d''$.
+·012
+·011
+·011 (4)
−·136

Line 4413·1 : $2p_2$–3S.
+·028 ; −·015
+·028 ; ——
+·028 (1) ; −·015 (3)
−·144 ; +·077

Line 3499·9 : $2p_2$–3D.
+·018 ; −·010
+·016 ; ——
+·017 (2) ; −·010 (4)
−·139 ; +·082

Note.—Many times during this investigation the fringes of 6438·5 were beautifully clear and distinct. Several times this line was inspected with care, and it always appeared single.

The intensity estimates were made by comparing, under a low-power binocular microscope, the density of the components with the densities of a series of spectrograms taken with a slit-width about equal to the width of a fringe and with exposure times varying from 1 to 10. The density of the lines of the spectrogram varied over such a range that in most cases a line could be found in the spectrogram of exposure 10 which was of the same density as the main component of the cadmium line under observation. In this case the number to be assigned to the intensity of a weaker component was found with ease. While these estimates represent fairly well the relative intensities of the components as the light strikes the photographic plate, it must be borne in mind that the actual relative emission intensities may be something quite different because of the strong absorption of the subordinate series lines and the incipient reversal of the strong component of each.

In the following tables a component marked +·077 (2) is a component which is ·077 A.U. away from and on the long wave-length side of the strongest component of the line observed and has an intensity of 2 as compared with 10, the intensity assigned to the strongest component.

Table IV. has been added for the sake of completeness and to have the data handy for considerations taken up in Part II.

TABLE IV.

Fine Structure of other Cadmium Lines.

Wave-length.	Classification.	Remarks.
3261·0	$1S\text{-}2p_2$	Double, $\Delta\lambda - \cdot 019$ (2), $\Delta\nu + \cdot 179$. Wood [1].
2288·0	1S–2P	Double, $\Delta\lambda + \cdot 021$ (10), $\Delta\nu - \cdot 400$. Wood [1]. or $-\cdot 017$ (10) or $+\cdot 324$.
6438·5	3P–3D	Single. Michelson, Fabry and Perot, Hamy [2], Janitzki [3].
6325·2	$2P\text{–}3d'$	Double (no separation given). Hamy [2], Janitzki [3].
5154·7	2P–3S	Single. Hamy [2], Janitzki [3].
4664·5	2P–4D	Single. Hamy [2], Janitzki [3].

[1] Wood, *suprà*, p. 611.

[2] Hamy, *C. R.* cxxx. p. 489 (1900).

[3] Janitzki, *Ann. d. Phys.* xix. p. 36 (1906); xxix. p. 833 (1909).

Remarks on Reproductions. (Fig. 2, Pl. XII.)

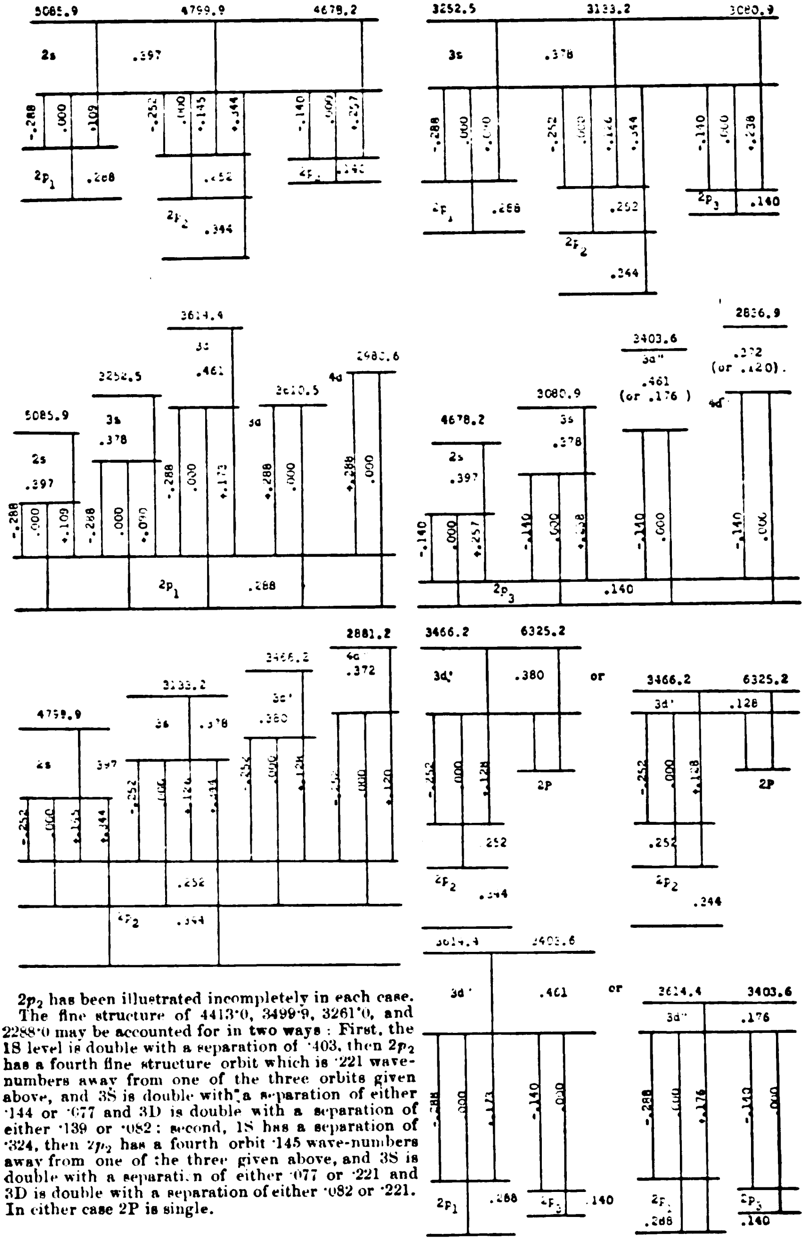
In preparing the reproductions an attempt has been made to show the existence and position of each component; consequently the contrast has been developed as much as possible, so that no great importance can be given the relative intensities of the fringes as reproduced.

5085·9 (Thick plate).	The main component appears reversed in two orders. The other lines appearing are 4799·9 and 4678·2.
4799·9 (Thick plate).	Two components shown by the thin plate are overlapped and shown as one fringe by the thick plate. 4678·2 appears also.
4678·2 (Thin plate).	4799·9 appears also.
4413·1 (Thin plate).	The −·015 component is unresolved from the main component.
3614·4 (Thick plate).	3610·5 and 3612·9 appear here very much over-exposed.
(Thin plate).	3610·5 and 3612·9 have been partially cut away.
3610·5 (Thin plate).	3612·9 and 3614·4 appear also.
(Thick plate).	3612·9 and 3614·4 have been cut away.
3499·9 (Thin plate).	The −·010 component is unresolved from the main component.
3466·2 (Thick plate).	3467·8 appears also.
(Thin plate).	3467·8 has been partially cut away.
3252·5 (Thin plate).	The edge of 3261·0 appears.
3133·2.	Two components shown by the thin plate are overlapped and shown as one fringe by the thick plate.
3080·9 (Thin plate).	3138·2 appears also.
2980·6 (Thin plate).	2981·3 and 2981·9 appear also.
(Thick plate).	2981·3 and 2981·9 have been cut away.
2881·3.	The reproduction of this line is not as satisfactory as the others, so it has been omitted.

PART II.

An attempt has been made to account for all the observed fine structure of the lines by assigning a certain fine structure to each level. Fig. 3 shows the result of such an attempt. The separations of the fine structure levels of any one level have been adjusted from the separations observed in all the lines starting or ending on that level. The separations are expressed in wave-numbers to the third decimal place, which, in most cases, implies an accuracy higher than that actually attained. The separations assigned to the p levels are slightly different from those assigned by Joos (*loc. cit.*), and $2p_2$ is more complex. 3403·6 may originate from the upper $3d''$ level and 2836·9 from the upper $4d''$ level. 4D and 4S need not be anything but single, though they may be double with a selection principle operating. Numbers can be assigned to the fine structure orbits, and an arbitrary selection principle stated so as to allow only those lines which appear.

Fig. 3.



$2p_2$ has been illustrated incompletely in each case. The fine structure of 4413·0, 3499·9, 3261·0, and 2288·0 may be accounted for in two ways: First, the 1S level is double with a separation of ·403, then $2p_2$ has a fourth fine structure orbit which is ·221 wave-numbers away from one of the three orbits given above, and 3S is double with a separation of either ·144 or ·077 and 3D is double with a separation of either ·139 or ·082; second, 1S has a separation of ·324, then $2p_2$ has a fourth orbit ·145 wave-numbers away from one of the three given above, and 3S is double with a separation of either ·077 or ·221 and 3D is double with a separation of either ·082 or ·221. In either case 2P is single.

There may be some significance in the fact that certain sets of orbits are similar; for instance, $2s$ and $3s$, 1S, 3S and possibly 4S, $3d$ and $4d$, $3d''$ and $4d''$. It should be noted also that $2p_2$ is without doubt much more complicated than either $2p_1$ or $2p_3$.

The fine structure of the cadmium lines which has been observed may be almost as nicely accounted for by quite a different arrangement of the fine structure of the orbits. In this arrangement the following orbits are the same as in the previous arrangement: $2s$, $2p_1$, $2p_3$, 1S (double, with separation of either ·400 or ·324), $3d$, $4d$, and $3d''$ (double, with separations of either ·461 or ·176). The following orbits are single: $3d'$, $4d''$, 3S, 4S, 3D, and 4D. The $3s$ orbit is double with a separation of ·243, and $2p_2$ has five fine structure orbits separated as follows (starting with the separation of the highest two): ·254, ·123, ·141, ·080. With this set of fine structure orbits it is possible to account for all the components of the fine structure of the lines observed, except the double structure of 6325·2 and the +·095 component of 3252·5. Other possible objections may be that $2p_2$ is relatively too complicated, and the +·176 component of 3614·4 is accounted for by making $3d''$ double while the other higher orbits are single.

I am greatly indebted to Professor R. W. Wood, with whom I worked continuously for three weeks in order to learn the technique of the Lummer-Gehrcke plate, and who has given many suggestions concerning experimental procedure during the progress of the work.

The Johns Hopkins University,
Baltimore, Md.
June 18, 1926.

LV. *Note on some Observations of the Nitrogen Afterglow Spectra.* *By* R. C. JOHNSON, *B.A.*, *Ph.D.*, *and* H. G. JENKINS, *B.Sc.* (*Queen's University*, *Belfast*) *.

Introduction.

IT is very remarkable that there are so few molecules capable of yielding an afterglow emission. The familiar nitrogen afterglow is of course outstanding among these, and its nature and properties are well known to us through the work of Lewis [*], Rayleigh [†], and others on the experimental side, and that of Birge [‡] and many others from a theoretical standpoint. The spectrum of the nitrogen afterglow, consisting of the so-called α-, β-, and γ-groups, is partly in the visible region and partly in the ultra-violet. To be more precise, the group, which we believe originates from a metastable N_2 molecule, lies in the red, yellow, and green; the other groups, originating from a metastable NO molecule, are chiefly in the ultra-violet. It seems conceivable, therefore, that many molecules may radiate afterglows lying entirely in the ultra-violet, and unsuspected through having no visual accompaniment. We have made a systematic search in a number of typical cases, but with negative results. At the same time we have used the method described below to make an extensive series of observations of the nitrogen afterglow, and some of the facts—though mostly familiar through Rayleigh's work—were felt to be worth recording, especially as they have been the subject of controversy.

---

* Communicated by the Authors.

Experimental.

We have used a method the same in principle as that described by Lewis. An interrupter of the magnetic type was inserted in the primary circuit of the induction-coil. The interrupter used had three solenoidal coils corresponding to three prongs disposed at 120°, which made periodic contact with a mercury surface. A disk consisting of three sections of 60° angle was fixed to the axle of the interrupter and "tuned" so that observation of the light from the tube was possible only at the intervals when the discharge current was off (see fig. 1).

This method was found excellent for a search for afterglows in the ultra-violet, the light of the discharge-tube being photographed by a quartz spectrograph after passing hrough the disk. It also has a great many advantages over the stream method.

(1) A discharge-tube of practically any length may be used, and a light-source of high intrinsic value is thus available. It is suggested that this method will be found excellent when grating photography of the β-group for the purpose of fine-structure analysis is attempted.

---

[*] Ast. Journ. vol. xx. p. 50 (1904). Phil. Mag. (6) vol. xxv. p. 826 (1913).

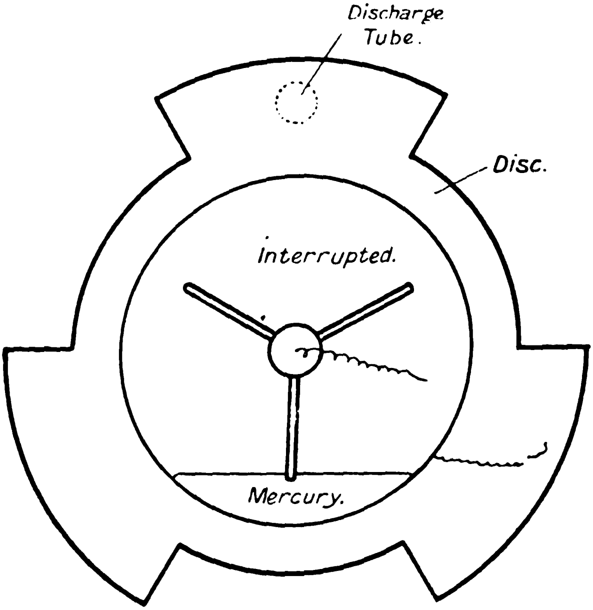
[†] Proc. Roy. Soc. A, vol. lxxxv. p. 377 (1911); vol. lxxxvi. p. 105 (1912); vol. xciii. p. 254 (1917), etc.

[‡] 'Nature,' Nov. (1924). Ast. Journ. vol. lv. p. 273 (1922). Phys. Rev. vol. xxiii. p. 295 (1924), etc.

(2) It permits of the detection and photography of afterglows of short duration.

(3) By adjustment of the speed of the disk and the use of suitably placed sectors, it should be possible to examine the afterglow spectrum at any particular time after its production. (This may be of some importance—as one of us has pointed out (Phil. Mag. vol. xlviii. p. 1069, 1924)—in connexion with the theory of the α-group "selection.")

Fig. 1.



The Nitrogen Afterglow.

The disk method permits of no possibility of stray light from the discharge giving spurious results, and definitely confirms Rayleigh's observations of the presence of many of the groups of the first positive band spectrum in addition to the enhanced "selection." It is equally certain that the second positive nitrogen bands are no part of the afterglow spectrum. In all our experiments we used glass tubes of the H type fitted with quartz window and side bulbs containing KOH and P_2O_5. Under these circumstances it was found that while the β- and γ-groups appeared along with the α-group immediately after having filled the tube, no trace of them was found after the discharge had passed for two or three hours, the oxygen impurity having presumably been removed as oxides of nitrogen into the potash. Such a tube was prepared and fitted with a side bulb containing $KMnO_4$ for the purpose of admitting oxygen. By admission of oxygen into the pure nitrogen, as produced above, the β- and γ-groups were stimulated with great strength. We found them of maximum strength when the α-group had been suppressed, and only a faint blue light (due to the less refrangible members of the β-group) was visible in the tube. Addition of a large amount of oxygen then produces the curious afterglow with a greenish-yellow continuous spectrum referred to by Rayleigh.

We have found that the best conditions for its production are a little nitrogen in a large quantity of oxygen. Photographs of its spectrum yield nothing notable except the continuous spectrum above λ 4300. The mercury line λ 2536 was notably absent in the presence of this spectrum, although it had been conspicuously strong a short time before in the nitrogen afterglow. This would seem to place an upper limit of 4·86 volts to the energy with which this curious afterglow molecule is loaded.

In view of Rayleigh's observations * on the modifications of the α-group in the presence of the inert gases, we have used the disk method to examine the β- and γ-groups under these circumstances. We have examined the nitrogen afterglow produced in the presence of high-pressure helium and argon, but there is no apparent change in the intensity distribution.

The Cyanogen "Tail" Bands.

On several of our plates a system of bands degraded to the red and described by Rayleigh † as "Tails" of the violet CN bands appears. Their presence was due to a trace of carbon contamination in the tube. Our observations of the intensity variations of the system with the CN bands leave no doubt as to its connexion with them.

In view of our knowledge of the spectra which originate from one-valence electron emitters of which CN is the prototype, it was thought of some importance to examine this system more closely to see whether there was any quantum theory relation between it and the two familiar spectra of CN. Table I. gives wave-length measurements of the bands on our plates, which are possibly correct to

---

* Proc. Roy. Soc. A, vol. cii. p. 453 (1923).

† Proc. Roy. Soc. A, vol. lxxxvi. p. 115 (1912).

TABLE I.

Int.	λ (IA).	Wave-no. *in vacuo.*	λ (IA) King.	Wave-no.	*n′*.	*n″*.
c.	4133·1	24188	—	—	11	13
3	4079·3	24507	—	—	10	12
5	4030·0	24807	—	—	9	11
8	3986·3	25079	3984·78	25088·4	8	10
8	3948·4	25319	3944·76	25342·9	7	9
8	3914·5	25539	3910·30	25566·3	6	8
7	3889·3	25704	—	—	5	7
v.c.	3869·8	25834	—	—	4	6
2	3693·4	27068	—	—	7	8
4	3663·2	27291	3658·19	27328·2	6	7
5	3635·4	27499	3628·91	27548·7	5	6
7	3612·9	27671	3602·97	27746·5	4	5
3	3542·7	28219	—	—	9	9
6	3502·0	28547	—	—	8	8
8	3466·1	28843	3465·54	28847·3	7	7
6	3433·8	29114	3433·03	29120·5	6	6
3 *c*	3407·2	29341	3404·90	29361·0	5	5
1	3386	29525	3380·44	29573·5	4	4
—	—	—	3360·13	29752·2	3	3
—	—	—	3340·50	29927·1	2	2
—	—	—	3322·26	30091·4	1	1
—	—	—	3296·34	30328·0	0	0
2 *d*	3262·2	30645	—	—	7	6
0	3231·9	30933	—	—	6	5
1	3204·9	31193	3203·71	31204·8	5	4
0	3182	31417	3180·45	31433·0	4	3
—	—	—	3160·19	31634·5	3	2
—	—	—	3142·93	31808·2	2	1
—	—	—	3127·87	31961·4	1	0

about 0·5 Ångström unit for the strong heads. Micrometer settings were made on the *edge* of each band, which probably accounts for the discrepancy between King's values and our own. In addition, the intensity distribution within the bands is different for their production in active nitrogen and in the carbon arc. King's observations* were made on the carbon arc. His values also are probably in error by a few tenths of an Ångström unit, as shown by an analysis of the corresponding wave-numbers. We have assigned vibrational quantum numbers tentatively, as indicated in Table I.; but these are subject to a measure of uncertainty, and a

* Ast. Journ. vol. 14 (1901).

closer examination of the bands as produced in the carbon arc would be desirable before calculating formulæ. It will be noted that King has observed a large number of heads at the more refrangible end of two of the groups, which we have not obtained in active nitrogen. If these are definitely present and a part of the system, they correspond to transitions from and to the states of small vibrational quantum number, and the first band observed in active nitrogen, λ 3182, would be the (4, 3) band. We have assumed that they are genuine in the above assignment of (n', n''). The distribution of energy among the vibrational states is then somewhat abnormal. The afterglow development is characterized by the absence of the initial states $n'=0$, 1, 2, and 3, and the final states $n''=0$, 1, and 2, and it is therefore notably a high temperature but non-thermal distribution. The production, under the arc conditions, of the early members of the sequences $\Delta n=0$ and $\Delta n=-1$ only $(\Delta n=n''-n')$ will then indicate, according to Lenz, comparatively little interaction between the emitting electron and the nuclear vibrations (*cf.* Mulliken's discussion of intensities in the spectra of BO, SiN, and CuI)*.

Altogether a much more critical examination of the system under arc conditions is desirable. Our analysis on the basis of available data makes it improbable, however, that it is related to either the violet or red CN systems. The possibility that it originates in ionized CN (*i.e.* CN^+) will have to be considered, though such a molecule would be of the inert gas type (*cf.* BN), and therefore difficult, if at all possible, to excite. On the other hand, CN probably has a very low ionization potential, for the initial state of the violet CN emitter is only 3·18 volts above the normal level. It is therefore not an impossible conjecture that active nitrogen may be capable of exciting CN^+.

The β-group of the Nitrogen Afterglow.

The so-called β-group, which occurs along with the γ-group or third positive bands of nitrogen in the afterglow, has been re-measured. Some good photographs were obtained by both the disk and stream methods, and Table II. records the wave-lengths measured, together with Rayleigh and Fowler's † values. We have extended the system at the less refrangible end, and have arranged it in series,

---

* Phys. Rev. vol. xxv. p. 259 (1925); vol. xxvi. p. 319 (1925); vol. xxvi. p. 1 (1925).

† *Loc. cit.*

TABLE II.

λ (IA).	Int.	Wave-no.	λ (Rayleigh).	Int.
5270·1 5252·7	00	18969·7 19032·4	—	—
4912·1 4892·1	2	20352·2 20435·4	—	—
4810·0 4791·4	1	20784·2 20864·9	—	—
4589·7 4572·5	5	21781·8 21863·8	—	—
4494·8 4479·1	3	22241·7 22319·7	—	—
4401·5 4385·7	2	22713·2 22795·0	—	—
4309·7 4293·7	3	23197·0 23283·4	4312·3 4296·5	1
4303·1 4288·2	3	23232·5 23313·3	—	—
4214·9 4199·8	4	23718·7 23804·0	—	—
4127·3 4113·0	4	24222·1 24306·3	—	—
4041·2 4027·2	6	24738·2 24824·2	4042·8 4028·7	2
3962·7 3949·7	2	25228·2 25311·2	—	—
3880·7 3868·3	5	25761·3 25843·8	—	—
3800·9 3788·0	10*c*	26302·1 26391·7	3801·9 3789·3	4
3647·0 3662·4	0*vc*	27210·6 27296·7	—	—
3658·4 3647·0	4	27326·6 27412·0	—	—
3583·2 3571·9	10*c*	27900·1 27988·3	3584·7 3572·9	6
3456·9 3446·0	2	28919·4 29010·9	—	—
3408·5 3398·9	1*c*	29330·0 29412·9	—	—
3386·0 3375·9	10	29524·9 29613·3	3387·2 3376·8	9
3364·3 3355·2	0	29715·5 29796·0	—	—
3340·3 3330·7	3	29928·8 30015·1	—	—
3298·6 3289·7	0*d*	30307·2 30389·2	—	—

TABLE II. (*continued.*)

λ (IA).	Int.	Wave-no.	λ (Rayleigh).	Int.
3206·9 3197·4	10	31173·8 31266·4	3207·4 3198·4	10
3168·4 3158·6	3 obsc.	31552·6 31650·5	—	—
3131·1 3125·0	2	31928·4 31990·8	—	—
3042·7 3034·3	10	32856 0 32947·0	3043·2 3035·0	10
3010·7 3002·8	1	33205·2 33292·6	—	—
2950·8 2943·2	3	33879·2 33966·7	2951·2 2944·0	2
2923·6 2915·6	4 *d*	34194·4 34288·2	2923·8 2916·2	2
2892·4 2884·8	10	34563·3 34654·3	2893·0 2885·4	9
2809·5 2802·4	4	35583·1 35673·2	2809·7 2802·7	2
2786·0 2779·5	3	35883·2 35967·1	2786·5 2780·1	2
2754·2 2747·3	9	36297·5 36388·6	2754·5 2747·9	7
2731·7 2725·4	1	36596·4 36681·0	2732·2 2726·0	1
2678·7 2672·2	7	37321·2 37410·5	2678·8 2672·9	3
2626·5 2620·4	6	38062·1 38150·7	2626·9 2620·9	4
2608·3 2602·1	6	38327·7 38419·0	2608·6 2602·9	2
2557·9 2551·8	5	39082·9 39176·3	2558·0 2552·3	2
2542·2 obsc.	2 —	39324·2 —	2542·8 2537·1	1
2528·7 2523·2	0 *d*	39534·1 39620·3	—	—
—	—	—	2509·0 2503·2	1
2493·4 2487·8	7	40085·7 40184·0	2493·9 2488·3	3
2433·0 2427·8	7 *d*	41089·0 41177·0	2433·2 2428·2	3
2386·4 2381·5	1	41890·5 41977·5	2387·0 2382·3	1
2331·4 2326·6	3	42879·5 42968·0	2331·5 2326·8	2
—	—	—	2236·1 2232·2	1

assigning vibrational quantum numbers (n', n''). The series denoted β, β_1, β_2, and β_3 by Rayleigh and Fowler are respectively given by $n'=0$, 1, 2, and 3. The whole arrangement is shown in Table III. The assignment of final quantum numbers was a matter of some difficulty at first. Birge and Mulliken[*] have stated, however, that the β- and γ-groups have the same final electronic state—which is the normal state of the NO molecule—so that the assignment of final quantum numbers to the third positive group is of assistance. No very good measurements of this group are available, and so the system was re-measured. It has not been thought necessary to reproduce these measures here. The use of Schumann plates made the measurement of the system possible down to λ 1900, and an analysis of these values gives the band at λ 2269 as the (0, 0) band of the system. A correct assignment of quantum numbers to the β-system has therefore been possible. With only four initial states a very accurate calculation of the coefficients of n' and n'^2 was not possible. We find, however, that the system is fairly represented by:

$$\nu=\left.\begin{matrix}46394\cdot6\\45485\cdot0\end{matrix}\right\}+(1029\,n'-7\cdot5\,n'^2)-(1889\cdot05\,n''-13\cdot96\,n''^2).$$

There is no doubt from our figures that the doublet separation is not constant through the spectrum. The separations for the β-series $(0, n'')$ are a function of n'', involving at least the first and second powers of n'', so that the formulæ for the two heads are really different. We have, however, used the same coefficients 1889·05 and 13·96 for both heads, and also the mean value (90·4 units) of the separation in the above formulæ. The error introduced by doing this is only small.

In connexion with the energy levels of the nitric oxide molecule, an interesting letter by Dr. Spooner has recently appeared in 'Nature,' Jan. 16th, 1926. From this it is apparent that λλ 2269 is the (0, 0) band of the third positive nitrogen system. In addition, the Birge-Hopfield bands in the region λλ 1854–1250 are found to have their final electronic state identical with the initial state of the third positive emitter. It seems possible, therefore, that there may be another band system found in the nitrogen afterglow—in the Schumann region—having for its initial state that of the Birge-Hopfield system, and for its final state the initial state of the β-group. This possibility would be worth investigating.

[*] 'Nature,' p. 349, Sept. 6th, 1924.

Table III.

n' n''.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.
			1791·7	1763·4	1736·6	1707·4	1681·4	1652·0	1624·9	1597·3	1566·2	1541·0	1508·5	1480·7	1450·1	1429·0	1403·0
0	- -	visible	(6) 38151	(9) 36388	(10) 34654	(10) 32947	(10) 31266	(10) 29613	(10) 27988	(10) 26392	(6) 24824	(3) 23283					
1021·5																	
1	—	trace	(5) 39176	(7) 37410	(4) 35673	(3) 33967	trace	—	(2) 29011	(4) 27412	(5) 25844	(4) 24206	(2) 22795				
1007·4																	
2	visible	(1) 41977	(7) 40184	(6) 38419	(1) 36681	—	—	—	—	—	—	(2) 25311	(4) 23804	(3) 22320	(1) 20865		
991·4																	
3	visible	(3) 42968	(7) 41177	obsc.	—	(3) 35967	(4) 34288	trace	—	—	—	—	trace	(3) 23313	(5) 21864	(2) 20435	(00) 19032

For the sake of simplicity, only the more refrangible member of each doublet is given in the above table. The other heads are found in Table II.

Intensity Distribution in the β-System.

In addition to the wave-numbers, Table III. records estimated intensities. A study of these presents some very remarkable features. A discussion of the distribution of intensity among the vibrational states has been made for BO, SiN, and CuI by Mulliken *, and for the β-group and other systems by Birge *. The distribution has been studied by these and other investigators as a function of n' and of Δn, and an advance on the theoretical side is due to Lenz †.

If the equilibrium is of a thermal type, then the distribution of energy among the initial states should be proportional to $e^{-\frac{E_n}{kT}}$, if E_n is the energy associated with vibrational quantum number n. It has then been customary to describe the type of energy distribution in a spectrum as a low temperature or a high temperature distribution according as the intensity "gradient"—as n' increases outwards from (0, 0)—is in conformity with a small or large value of T. The Ångström band system—with $n'=0$ and 1 only—is, for example, typically a low-temperature distribution. On the other hand, the term "high-temperature distribution" is very wide, and covers such vastly differing cases as the violet CN bands and extreme cases like the ultra-violet oxygen bands, in which the possibility of the distribution being thermal in origin at all is quite ruled out.

In the case of the β-group above, it is clear that we cannot describe the energy-distribution among n' values as characteristic of either "high" or "low" temperature. If the columns from $n''=7$ to 10 were alone present we might say it was "low," but for very small and very large values it is decidedly "high" temperature.

We wish, however, to draw attention to a characteristic type of energy distribution which is found in a great many spectra. It is more common as a type of distribution among the final vibrational states (n'') than among the initial states, although it is found in both. Dealing now only with the distribution among the final states, Table III. indicates a typical high temperature non-thermal distribution for $n'=0$ (using these terms for the sake of convenience). For $n'=1$ there is a characteristic "instability" of the final states which in $n'=0$ were the most probable. This is still more notable for $n'=2$ and 3, and the effect seems to widen almost symmetrically, about $n''=9$ in the above case. Other such cases may be noted, *e.g.* the high-pressure CO bands *, which are a single n'' sequence. The (0, 1) band is the strongest, (0, 2) is almost absent, while (0, 3), (0, 4), etc., increase in intensity. The A and E systems of the CuI molecule † show the effect well. The SO_2 bands ‡ also show the effect in a very striking manner. In the case of the third positive carbon bands we have found for the *initial* states that the sequence $n'=0$ is strong, $n'=1$ is faint, $n'=2$ and 3 are absent, and $n'=4$ is faint.

---

* *Loc. cit.*

† *Zeit. für Phys.* vol. xxv. p. 299 (1924).

Returning to the β-system with this typical distribution of intensity among the n'' states, we have not found it possible as yet to suggest any adequate cause. It seems possible, however, that the emitting electron in this case is exceedingly sensitive to perturbation arising from vibrational motion of the nuclei, so that some distinct internal change (such as a change of *type* of the electronic orbit) takes place if one quantum of vibration is acquired. This configuration change, whatever it be, is exaggerated for molecules existing with two vibrational quanta, and so on. Some such cause may account for the difference in behaviour of the $n'=0$ sequence from the others, $n'=1$, 2, and 3 ; but the origin of the instability of a number of the n'' states is very obscure, particularly as the n'' level of the β-system is the normal level. If there were a system in the infra-red having its final level in common with that of the β-group (*i. e.* the normal level), then the overlapping of the very extensive final vibrational levels of the β-group with the initial vibrational levels of this hypothetical system might account for the facts. This, however, seems unlikely for two reasons :

(1) The hypothetical system would need to extend into the visible region to account for the observed range of instability.

(2) Such an explanation is unlikely to hold generally, and the observed phenomenon is characteristic of a *class* of molecules.

It is perhaps worth noting that in the $n'=3$ sequence of the β-group (see Table III.) there is evidence of *two* minima in the intensity distribution among the n'' values.

The factors governing the distribution of energy among the vibrational states of a molecule provide a very big field of investigation both for the theorist and the experimental spectroscopist.

February 6th, 1926.

---

* Proc. Roy. Soc. A, vol. ciii. (1923), plate.

† Phys. Rev. vol. xxvi. diagram, p. 20 (1925).

‡ Proc. Roy. Soc. A, vol. cvi. p. 215 (1924), plate.

LVI. *On the Arc Spectrum of Lead.* *By* NALINI KANTA SUR, *M.Sc., University of Allahabad*[*].

1. INTRODUCTION.

KAYSER and Runge[†] were the first to note regularities in the arc spectrum of lead. Their results were extended by Saunders[‡], Zumstein[§], and Meissner[||], but the first important step towards the classification of the spectrum into series was taken by Thorsen[¶], who studied the arc spectrum of lead with quartz spectrographs of high dispersion, and was thus able to measure the wave-lengths of many weak lines not recorded before. From these data Thorsen identified the sharp and diffuse series characteristic of a triplet system, and found that the limits $2p_1$, $2p_2$, and $2p_3$ of these series had the separations 10810·8 and 2831·8 respectively, as found by Kayser and Runge.

The absorption spectrum of lead vapour was first studied by McLennan and Zumstein[**], and later on reinvestigated by Grotrian[††], and independently by Sur and Sharma[‡‡], up to a temperature of 1300° C. Grotrian, as a result of his absorption experiments at different temperatures, introduced another term $2p_4$ corresponding to the normal state of the atom. According to him the line $\lambda = 2833{\cdot}17$ Å., which is the first line to come out in absorption and which was not included in Thorsen's scheme, is produced by the combination of $2p_4$ with $2s$. This extension of Thorsen's scheme leads to the conclusion that $\lambda = 2170{\cdot}07$ Å., and $\lambda = 2053{\cdot}83$ Å., which satisfy the combinations $2p_2 - 3d_2$ and $2p_4 - 3s$ respectively, should also be absorbed simultaneously with $\lambda = 2833{\cdot}17$ at the same temperature. Grotrian was unable to obtain these lines in absorption, but the simultaneous absorption of $\lambda = 2833{\cdot}17$ Å. and $\lambda = 2170{\cdot}07$ Å. at the same temperature was noted independently by Sur and Sharma[§§], who, as well as Grotrian, were unaware of the work of McLennan and Zumstein [*], who had previously found that the lines $\lambda=2170{\cdot}07$ Å., $\lambda=2053{\cdot}83$ Å., $\lambda=2833{\cdot}17$ Å. and $\lambda=2022{\cdot}64$ Å. were absorbed by normal lead vapour at a temperature of 750° C. Two other combination lines, $\lambda=1868{\cdot}7$ Å., $\nu=2p_4-4s$, and $\lambda=1904{\cdot}9$ Å., $\nu=2p_4-4d_1$, previously observed by Saunders [†], justified the existence of the $2p_4$ term, and McLennan, Young, and McLay [‡], as a result of their investigation of the lead arc-spectrum with a fluorite spectrograph, have made important verifications of the Thorsen–Grotrian Scheme by identifying nineteen more combinations.

---

[*] Communicated by Prof. M. N. Saha, D.Sc., F.I.P.

[†] Kayser and Runge, *Handbuch der Spectroscopie*, Bd. ii. p. 574.

[‡] Saunders, Astrophys. Journ. xliii. p. 240 (1916).

[§] Zumstein, Trans. Roy. Soc. Canada, Sec. iii. 59 (1918).

[||] Meissner, *Ann. der Phys.* lxxi. p. 135 (1923).

[¶] Thorsen, Naturwissenchaften, xi. p. 78 (1923).

[**] McLennan and Zumstein, Trans. Roy. Soc. Canada, Sec. iii. 9 (1920).

[††] Grotrian, *Zeits. f. Phys.* xviii. p. 169 (1923).

[‡‡] Sur and Sharma, Journ. of the Science Association, Marahajah's College, Vizianagram, J. 1, No. 4, pp. 121–124 (1924). Also Science Abstracts, xxviii. p. 43 (1925) (Abstract No. 126).

[§§] Sur and Sharma, *loc. cit.*

To account for the absorption of $\lambda=3683{\cdot}47$ Å. at a temperature of 1000° C., the $2p_5$ term was introduced by Grotrian. The combinations with $2p_5$ are very few in number, and Zumstein [§] concludes, from a later absorption experiment at high temperatures, that it is unnecessary to introduce the $2p_5$ term, and that $\lambda=3683{\cdot}47$ Å. is the first line of a series designated by him as the $2p_3-mx$ series, the separation between $2s$ and $2x$ being 327, as noted by Saunders [‖] and Meissner [¶]. In the same work, Zumstein suggests that $\lambda=10650{\cdot}8$ and $\lambda=6011{\cdot}76$ may be $2s-3p_2$ and $2s-4p_2$ combinations respectively, and, further, $\lambda=10291{\cdot}3$ Å. and $\lambda=5895{\cdot}68$ Å. may be the $2x-3p_2$ and $2x-4p_2$ combinations. If this is true, then higher members of these two series should be obtained in the region of spectrum $\lambda=6000$ A.—$\lambda=4000$ Å. This suggested a reinvestigation of the arc lines of lead in that region, and many new lines of lead have been obtained as reported below.

But before passing on to the results of the present investigation, it is necessary to mention the important results obtained by Gieseler and Grotrian [**] in a recent work on the series classification of the arc-spectrum of lead, which came to hand during the course of the present work. These authors have excited the spectrum in the presence of a dense rain of electrons, after the method of Whiddington [††] for exciting the higher members of the Balmer series of hydrogen, and have thus obtained some higher members of the series previously classified by Thorsen and by Grotrian himself, and also many new lines not recorded by previous observers. As they have recorded their results in terms of the new notation given by Sponer [*], the relation between the new and old systems of notation is shown in the following scheme. From the different combinations Sponer has fixed the inner quantum numbers of the various terms, and following Sommerfeld has named them accordingly. Thus :—

---

[*] McLennan and Zumstein, *loc. cit.*

[†] Saunders, *loc. cit.*

[‡] McLennan, Young, and McLay, Trans. Roy. Soc. Canada, Sec. iii. xviii. p. 77 (1924).

[§] Zumstein, Phys. Rev. xxvi. p. 189 (1925).

[‖] Saunders, *loc. cit.*

[¶] Meissner, *loc. cit.*

[**] Gieseler and Grotrian, *Zeits. f. Phys.* xxxiv. p. 374 (1925).

[††] Whiddington, Phil. Mag. xlvi. p. 605 (1923).

Thorsen-Grotrian...	p_4	p_3	p_2	p_1	$3d_1$	$3d_2$	$3d_3$	$4d_3$.
Sponer	p_0	p_1	p_2	P_2	$3d_3$	$3d_1$	D_2	D_2.
Gieseler-Grotrian ..	p_0	p_1	p_2	P_2	$3d_3$	$3d_1$	$3d_2$	$4d_3$.

In the new system, the suffixes denote the inner quantum numbers of the different terms. As shown in the above scheme, Sponer assigns the inner quantum number 2 to both the $3d_3$ and $4d_3$ terms, but Gieseler and Grotrian, for reasons mentioned in their paper, call it $3d_2$ and $4d_2$ terms respectively. Adopting this notation, Gieseler and Grotrian have shown that three higher members of each of the series P_2-ms, p_2-md, and P_2-md_1, one member of each of the series p_2-md_2, P_2-md_3, and p_2-md_3 series, and two members of the series P_2-md_3 are obtained from the new lines recorded by them. They have been further able to identify the series p_2-mf_3, P_2-mf_3, P_0-ms, and P_0-md, and have thus definitely established the existence of a fifth P term, as is to be expected from the theoretical work of Pauli [†] and Heisenberg [‡], Goudsmit [§], and Hund [||].

2. Experimental Method.

The arc-spectrum of lead was excited by the method of Hemsalech and de Gramont [¶]. The positive pole was a thick copper plate, about 10 by 5 cm. in area, with a small depression in it to contain the molten lead. For the negative pole a rod of Acheson graphite was used, so that the impurities in ordinary carbon were avoided to a very large extent. A current of about 25 amperes was sufficient to produce a dense vapour of lead in the arc, the spectrum being photographed in the first order spectrum of a 5-foot concave grating, with a dispersion of 11·12 Å. per mm. Photographs were taken on Lumière S.E. orthochromatic plates, these being specially sensitive to green and yellow regions of spectrum, and exposures of at least twenty minutes were necessary to record the faint lines. Six plates were measured with a Hilger comparator, and the wave-lengths were interpolated in the usual manner, with reference to standard lines of iron. Unfortunately, the wave-lengths are not as accurate as desired, as the average error could not be reduced below ·05 Å., and in the case of very faint lines, designated with intensity 0, the error is about ·08 Å. The existing tables of the wave-lengths for bismuth, zinc, cadmium, silver, copper, tin, silicon, aluminium, arsenic, sodium, potassium, phosphorus, and antimony were compared to eliminate the lines due to possible impurities, as chemically pure lead was not available. The wave-lengths of the lines measured are given in Table I.,

---

[*] Sponer, *Zeits. f. Phys.* xxxii. p. 19 (1925).

[†] W. Pauli, Jr., *Zeits. f. Phys.* xxxi. p. 765 (1925)

[‡] Heisenberg, *Zeits. f. Phys.* xxxii. p. 841 (1925).

[§] Goudsmit, *Zeits. f. Phys.* xxxii. p. 794 (1925).

[||] Hund, *Zeits. f. Phys.* xxxiii. p. 345 (1925).

[¶] Hemsalech and de Gramont, Phil. Mag. xliii. p. 291 (1922).

Table I.

I.A.	Int.	Wave-number.	Remarks.
5818·56	1	17181·6	
5750·99	0	17383·5	
5743·47	0	17406·3	
5738·40	0	17421·6	
5727·03	4	17456·3	
5703·52	3	17528·2	
5692·20	8	17563·0	Walters (5692·26), Eder and Valenta.
5670·81	2	17629·3	
5608·87	8	17824·0	Walters (5608·85), Eder and Valenta.
5603·40	4 h	17841·4	
5598·76	4	17856·2	Cd ?
5594·20	5	17870·7	
5588·68	6	17988·4	
5534·74	3	18062·7	
5513·53	3 h	18132·2	
5459·3	0 h	18312	
5407·1	0 h	18489	
5372·5	0 h	18608	
5256·9	0	19017	
5241·48	1	19073·3	
5224·25	5	19136·2	Sn ?
5210·26	2	19187·6	Recorded in Kayser's *Handbuch der Spectroscopic*, vol. vi.
5206·34	1	19202·0	
5201·47	10	19219·9	Recorded in Kayser's *Handbuch der Spectroscopic*, vol. vi.
5173·01	3	19325·7	
5164·84	1 h	19356·3	
5163·67	1	19361·8	G.
5116·93	0	19537·5	
5108·62	4	19569·3	G.

TABLE I. (*continued*).

L.A.	Int.	Wave-number.	Remarks.
5090·65	8	19638·4	G.
5086·73	0	19653·5	
5077·35	1	19689·8	G.
5064·02	4	19741·7	
5043·57	1	19821·7	Obtained by Gieseler and Grotrian only.
5035·65	4	19852·9	
5024·43	3	19897·3	
5019·34	1	19917·4	
5005·45	10	19972·7	Recorded in Kayser's list.
4999·36	4	19997·0	
4981·30	6	20069·5	G, but measured as 4980·96.
4962·21	2	20146·7	
4900·21	2	20401·6	
4885·00	3	20465·1	
4875·71	4	20508·3	
4870·31	2	20526·9	
4864·95	3	20549·5	
4851·15	2	20607·9	
4831·66	2	20691·1	
4826·98	2	20711·1	
4820·25	1	20740·0	
4810·71	1	20781·2	Obtained by Gieseler and Grotrian only.
4723·68	3	21164·0	G.
4720·17	2	21179·8	G.
4718·59	1	21186·9	G.
4685·23	0	21337·7	Obtained by Gieseler and Grotrian only.
4680·62	0	21358·7	Obtained by Gieseler and Grotrian only.
4676·68	0	21376·7	Obtained by Gieseler and Grotrian only.
4664·86	3	21430·6	Obtained by Gieseler and Grotrian only.
4664·66	3	21514·7	G.
4618·21	2	21647·4	G.
4607·77	1	21696·4	Obtained by Gieseler and Grotrian only.
4602·52	4	21721·2	G.

"h" denotes that the line is hazy.

and it is rather surprising that so many new lines could escape the notice of the previous observers; but it may be mentioned here that Thorsen, McLennan and his co-workers, Gieseler and Grotrian, have also obtained many lines not previously recorded, and it seems that the arc-spectrum of lead still requires investigation in certain regions, which is being carried on.

3. RESULTS.

The lines of the arc-spectrum of lead, measured within the range of the spectrum $\lambda=4600-\lambda=5800$ Å., are noted in Table I. Reference is given to the lines, either previously recorded or recently by Gieseler and Grotrian, in the column under remarks. The lines marked "G" denote that they have been recorded and measured by these observers also. The intensities were visually estimated, and are only true locally. Table II. contains all the pairs of

TABLE II.

	λ I.A.	Int.	Wave-number (vac.).	Diff.	λ. I.A.	Int.	Wave-number.	
1	13101·9	40	7630·5	326·7	12563·8	40	7957·2	
2	10650·8	60	9386·4	327·9	10291·3	100	9714·3	
3	6235·44	4	16032·3	328·3	6110·70	3	16360·6	
4	6011·98	5	16629·5	327·4	5895·70	6	16956·9	
5	5703·52	3	17528·2	328·0	5598·76	4	17856·2	cd ?
6	5173·01	3	19325·7	327·8	5086·73	0	19653·5	
7	5163·67	1	19361·8	328·0	5077·35	1	19689·8	
8	5108·52	4	19569·7	327·6	5024·43	3	19897·3	
9	5064·02	4	19741·7	327·8	4981·30	6	20069·6	
10	4718·59	1	21186·9	327·8	4646·66	3	21514·7	
11	4602·52	4	21721·2	328·6	4533·92	2	22049·8	Obtained from Gieseler and Grotrian's data of new wave-lengths.
12	4582·9	0 u	21814	328·2	4515·01	3	22142·2	
13	2686·68	1	37209·6	328·5	2663·19	3	37538·8	
14	2658·94	1	37597·8	327·2	2636·00	1	37925·0	
15	2660·91	3	37570·0	329·3	2637·39	4	37899·3	
16	2066·43	0	48377·1	328·3	2052·50	0	48705·4	

lines having a separation of 328. These pairs have been tabulated from the data of the present writer, of Gieseler and Grotrian, and of previous observers. The first two pairs of wave-lengths of Table II. are noted in Rowland units, and have not been converted to international units, as the error in measurement exceeds the magnitude of the correction involved.

From Table II., it will be seen that there are four pairs of wave-lengths, with a separation of 328, which very approximately follow a Rydberg sequence. These are shown in Table III.

Table III.

$2s=24536 \quad 2x=24864.$

m.	$2s-mp_2$.	$2x-mp_2$.	mp_2 (observed).
			$2p_2=49173$
3......	$\lambda=10650{\cdot}8$ (60) $\nu=9386{\cdot}4$	$\lambda=10291{\cdot}3$ (100) $\nu=9714{\cdot}3$	15149·6
4......	6011·98 (5) 16629·5	5895·70 (6) 16956·9	7906·5
5......	5108·52 (4) 19569·7	5024·53 (3) 19896·8	4966·3
6......	4718·58 (1) 21186·9	4646·66 (3) 21514·7	3349·1

The observed value of the limit $2s$ is obtained from the combinations $2p_0-2s$, $2p_1-2s$, $2p_2-2s$, $2P_2-2s$, the values of the terms $2p_0$, $2p_1$, $2p_2$, $2P_2$ being 59821, 52004, 49173, 38365 respectively. These values are taken from Gieseler and Grotrian's paper, as they have been able to calculate more accurately the limits by exciting and measuring the wave-lengths of the higher members of the different series. The value of the term $2s$ as calculated by Gieseler and Grotrian is 23300, whereas the approximate value of the limit $2s$ calculated from the last two lines of the series $2s-mp_2$ is 24599, which closely agrees with the observed value 24536. The formula calculated from the last three lines of the series $2s-mp_2$ is

$$\nu=24703-\frac{N}{\left\{m+430251+\frac{\cdot 766215}{m}\right\}^2}(m=3,\ 4,\ 5).$$

The correcting term is unusually large, so that the series does not closely follow a Rydberg formula.

From Table II., it can be further seen that there are three more pairs of wave-lengths with a separation of 328, which also closely follow a Rydberg sequence. These are shown in Table IV.

TABLE IV.

$2s=24536$; $2x=24864$.

m.	$2s-mp_1$.	$2x-mp_1$.	mp_1.
3......	$\lambda=$ 13101·9 (40) $\nu=$ 7630·45	12563·8 (40) 7957·2	$2p_1=$ 52004 $3p_1=$ 16905·5
4......	6235·44 (4) 16032 3	6110·70 (3) 16360·6	$4p_1=$ 8503·7
5......	5173·01 (3) 19325·7	5086·73 (0) 19653·5	$5p_1=$ 5210

The approximate value of the term $2s$ as calculated from the last two lines of $2s-mp_1$ and Rydberg's table is 24522. The calculated values 24599 and 24522 are in close agreement with the observed value 24536. The higher members of the series $2s-mp_1$ and $2x-mp_1$ have not yet been obtained, and one can only be sure about the correctness of the allocation of the lines to the series when they are discovered.

It will be noted that the third member of the series $2x-mp_1$ $\lambda=5086{\cdot}73$ (I.A.) is very faint. It may be mentioned in this connexion that Gieseler and Grotrian * have recorded some anomalies in the intensities of the lines of some of the series of the arc-spectrum of lead. For example, the line $\lambda=5201{\cdot}467$ (3) (I.A.) P_0-3s is distinctly weaker than the line $\lambda=4157{\cdot}826$ (5) (I.A.) P_0-4s. Some other irregularities in the intensities of the lines have also been mentioned by them.

There are two interesting inter-combination lines which have not been noted previously. The line $\lambda=7330{\cdot}12$ (2) (I.A.), $\nu=13638{\cdot}59$ is the combination $2p_1-2P_2$ ($52004-38365=13639$), and the new line $\lambda=4618{\cdot}21$ (2) (I.A.), $\nu=21647{\cdot}4$, recorded both by Gieseler and Grotrian and the present writer, is the combination $2p_1-2P_0$ ($52004-30355=21649$). The difference between the observed and calculated wave-numbers in the latter case does not exceed the uncertainty in the value of the limit $2P_0$, as calculated by Gieseler and Grotrian from the new series P_0-ms and P_0-md_1, identified by them.

---

* Grotrian and Gieseler, *loc. cit.* p. 386.

From the new lines recorded and measured by Gieseler and Grotrian in the ultra-violet region, we also find four pairs of wave-lengths with a separation of 10806·6 as follows :—

	λ (I.A.).	Int.	ν.	Δν.	λ (I.A.).	Int.	ν.
1 ……	2052·50	(0)	48705·4	10806·1	2637·79	(4)	37899·3
			$\Delta\nu=328{\cdot}3$				$\Delta\nu=329{\cdot}3$
2 ……	2066·43	(0)	48377·1	10807·1	2660·91	(3)	37570·0
3 ……	2060·52	(2)	48515·8	10806·1	2651·07	(4)	37709·4
4 ……	2061·82	(1)	48485·3	10806·8	2653·24	(5)	37678·5

According to Gieseler and Grotrian, the separation between the values of the calculated limits $2p_2=49173$ and $2P_2=38365$ is 10808 ; hence the above lines can be represented as

$$\left.\begin{matrix}2p_2\\2P_2\end{matrix}\right\}-467{\cdot}6,\quad \left.\begin{matrix}2p_2\\2P_2\end{matrix}\right\}-795,$$

$$\left.\begin{matrix}2p_2\\2P_2\end{matrix}\right\}-657{\cdot}5,\text{ and }\left.\begin{matrix}2p_2\\2P_2\end{matrix}\right\}-687{\cdot}5$$

Now the second terms have very small values. The lines can therefore be either some higher members of some series, or may form a negative sequence analogous to the lines, discovered by Russell and Saunders * in the arc-spectrum of calcium. The first alternative does not fit in the scheme for the known series converging to either $2p_2$ or $2P_2$, and to test the second, further data are necessary, the region of the spectrum in which the expected lines are to be found being not yet explored.

It will also be noted that the separation 328 occurs in the first two pairs of lines of the above scheme. As it has not been yet possible to ascertain either the nature of the $2x$ term, or the significance of the separation $2s-2x$ occurring in other pairs of lines noted in Table II., it is difficult to decide whether this agreement of separation is real or accidental.

Finally, it may be mentioned that according to the scheme of the constitution of the arc-spectrum of the elements, carbon, silicon, germanium, tin, and lead of the fourth group of the periodic table, as discussed by Hund †, one of the five p-terms as given in the Thorsen-Grotrian scheme may be a D-term, and the other may be a S-term belonging to the

---

* Russell and Saunders, Astrophys. Journ. lxi. p. 38 (1925).

† Hund, *Zeits. f. Phys.* xxxiv. p. 301 (1925).

singlet system. If we identify the P_2 term with ${}^1D_2$ term and P_0 term with ${}^1S_0$ term (Notation of Russell and Saunders), then the lines $\lambda=7330{\cdot}12$ and $\lambda=4618{\cdot}21$ correspond to the inter-combinations ${}^3p_1-{}^1D_2$ and ${}^3p_1-{}^1S_0$ respectively; but there are other difficulties in reconciling this assumption with the relations which are already known to exist.

SUMMARY.

With a view to obtaining the higher members of the Rydberg sequence in the series spectrum of lead, the spectrum has been reinvestigated, using the heavy-arc method of Hemsalech and de Gramont. Several members of the series $2s-mp_{1,2}$ and $2x-mp_{1,2}$ have been obtained. Indications have been obtained that the arc-spectrum of lead contains negative terms, similar to those discovered by Russell and Saunders in the arc-spectrum of calcium, and ascribed by them to the simultaneous excitation of the two outer electrons. Two combination lines between the principal terms have been obtained.

In conclusion I wish to record my best thanks to Prof. M. N. Saha for his guidance and interest in the work.

March 3, 1926.

LVII. *Scattered X-Rays. The J Phenomenon* (Part IV.).

By Prof. C. G. BARKLA. *F.R.S., and* Dr. S. R. KHASTGIR, *University of Edinburgh* *.

INTRODUCTION.

IN a previous paper † we showed that when a heterogeneous X-radiation was scattered, the primary and scattered radiations had either { (1) exactly equal absorbability, or (2) markedly different absorbability, when measured in any particular substance. The one was an unmodified, the other a modified scattered radiation. In these results we found no support whatever for Compton's theory of quantum scattering. In every feature the difference observed between the primary and scattered radiations, when it appeared, was found to be due to what we have called the

---

* Communicated by the Authors.

† "The J Phenomenon in X-Rays.—Part II. Application to Scattered X-Rays," Phil. Mag. November 1925. See also Barkla and Mackenzie, "Notes on the Superposition of X-Rays and on Scattering. The J Phenomenon (Part III.)," Phil. Mag. Feb. 1926, and 'Nature,' Feb. 13, 1926.

J phenomenon. We showed, and we now propose to show more completely, that the difference observed depends upon the material used to test the radiation, *i. e.* upon the material used to compare the primary and secondary radiations.

Thus the difference between the scattered radiation and the primary as observed by us, is not a difference of wave-length as generally understood. It is a difference in the properties of the two radiations such as we are quite familiar with not only between a primary and scattered radiation, but under certain conditions between (*a*) two primary beams proceeding from the same source in different directions; (*b*) between two scattered radiations proceeding from the same source in slightly different directions; (*c*) it is a difference such as under suitable conditions occurs between either a primary or scattered radiation, and the same radiation subsequent to the slightest amount of filtering; (*d*) it is a difference such as appears under suitable conditions in a beam when a very feeble radiation is added to it *. These are not differences in the length of waves, and though the difference we have observed (when it appears) is of the magnitude to be expected on Compton's theory for wave-lengths in the neighbourhood of that of Mo 'K' radiation, this agreement is not general. In fact, beyond this chance agreement a comparison of our experimental results with Compton's is rather a comparison of contrasts. It is natural then to suggest that the occurrence of the J phenomenon in the scattered radiation is quite distinct from Compton's change of wave-length on re-emission (so-called scattering). But different though the Compton effect and the J-transformation are, both in the laws governing them and in the principles apparently underlying them, there is a correspondence between them which is too remarkable to admit of their independence. In addition, apart from the J-transformation of the scattered radiation, no evidence of the Compton change of wave-length appears in our experiments; it is simply not there. It should be remembered, however, that (1) we have experimented upon the scattering of heterogeneous beams, and (2) we have measured absorbability of radiations instead of an angle of diffraction, *i. e.* an angle at which tertiary rays appear from a crystal. The advantages of our method have already been stated.

This paper is principally concerned with three points:—(1) We show quite definitely that while the secondary differs from the primary radiation when its absorbability is examined in certain substances, it is precisely like the primary when its absorbability is measured in other substances. In other words, what to some substances is a modified scattered radiation is to others an unmodified radiation.

---

* (*e*) and it is possibly, though not so certainly, a difference such as occurs between two characteristic radiations from the same substance under slightly different conditions.

It was indeed shown in a previous paper that a difference between primary and secondary radiations appeared over very limited ranges of wave-lengths when measured in one substance, while there was no difference when measured in another substance. This, however, is more convincingly shown by the experiment described below. This cannot be reconciled with a change of wave-length on scattering, for that might be expected to be shown by absorption in *all* substances.

(2) This seemed to suggest the possibility of a change of wave-length occurring in the scattered radiation, not in the process by which it originated, but later when passing through the testing substance which exhibits the difference of absorbability. We therefore pursued the matter further and found that even after a difference between secondary and primary had been demonstrated in one substance, there was no difference between primary and secondary when tested by certain substances placed behind the first. That is, although the second substance *may* show the difference between primary and secondary radiations, it does not do so necessarily, for each testing substance has its own critical condition. We are therefore justified in saying that there is in our experiments no evidence of change in wave-length either in the process of re-emission or in the subsequent transmission through matter.

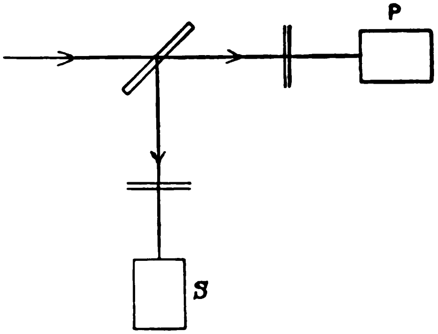
(3) Further, we have found no gradual variation of absorbability of a scattered radiation with the angle of scattering such as Compton's theory indicates. Frequently, no difference appeared between two radiations scattered at different angles. Where, however, a difference did appear, while it was in the right direction, it was the very precise difference which characterizes a "J discontinuity"; it was the familiar step between radiations on two sides of such a discontinuity; it was the difference between two well-defined absorption levels.

EXPERIMENTS.

Dependence on Testing Substance.

The ratio of the ionizations produced in two similar electroscopes by the secondary and primary beams was observed, first when the beams were unintercepted and subsequently when intercepted by similar sheets of any particular substance (fig. 1). As previously indicated, the "intercepted ratio" S′/P′ is frequently less than the "unintercepted ratio" S/P, because of the greater absorbability of the secondary beam; and as the thickness of the absorbing sheets is increased the ratio S′/P′ falls. Plotting S′/P′ against the thickness of absorbing substance, we thus get a curve sloping down to the right. A horizontal line would indicate equal absorption of secondary and primary radiations. Such a line is frequently obtained *; it indicates unmodified scattering, Now observe the results obtained and indicated in fig. 2 and Table I.. when the absorbing substances were aluminium, copper, silver, tin. It should be noticed that equal distances along the horizontal axis represent approximately equivalent thicknesses of the various absorbing substances for a 50 per cent. absorption of the original unfiltered beam, *i. e.* ·045 cm. of Al, ·0015 cm. of Cu, ·002 cm. of Ag, and ·0025 cm. of Sn were approximately equivalent in absorbing power, as measured by a short air electroscope. Observing the two upper curves, it will be seen that aluminium and copper indicated quite consistently that the secondary (scattered) radiation was more absorbable than the primary—S′/P′ steadily diminished by transmission, and by the same amount in the two substances. They thus gave consistent results indicating a modified scattered radiation. But from the third line it is seen that when measured in silver the secondary and primary radiations were identical: they were cut down to exactly the same extent by equal absorbing sheets, and the ratio S′/P′ remained constant and equal to S/P. Thus in aluminium and

Fig. 1.



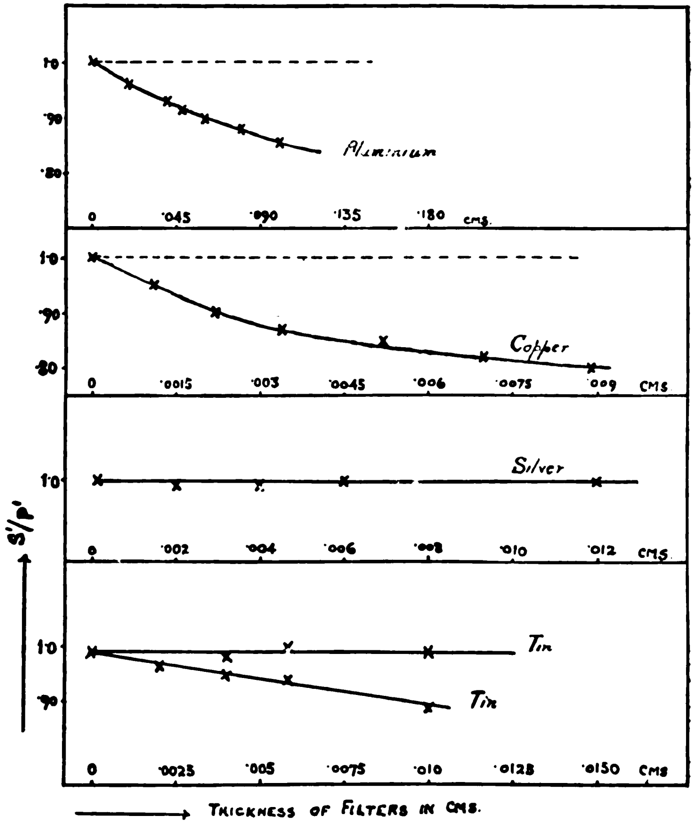
---

* Illustrated in previous papers.

copper the difference between secondary and primary was shown very markedly; in silver it did not appear at all.

Fig. 2.

Showing that what to Al and Cu is a modified scattered radiation is to Ag an unmodified radiation, and to Sn is sometimes one, sometimes the other.



Further, when tin was used the difference between secondary and primary appeared in some observations but not in others; and the various observations showed either no difference between secondary and primary or the well-marked difference *. The difference when it appeared was approximately half that shown by aluminium and copper.

---

* Bracketed numbers in Table I. show the order in which observations were taken.

TABLE I.

Absorbing substance.	Thickness of Absorbers.	Observed ratio $\frac{\text{Secondary}}{\text{Primary}}$ (arbitrary units).
Aluminium.	0·0 cm.	1·00 $\times x$
	·02 ,,	·96 ,,
	·04 ,,	·93 ,,
	·048 ,,	·91 (5) ,,
	·06 ,,	·90 ,,
	·08 ,,	·88 ,,
	·10 ,,	·85 (5) ,,
Copper.	0·0 cm.	1·00 $\times x$
	·0011 ,,	·95 ,,
	·0022 ,,	·90 ,,
	·0034 ,,	·87 ,,
	·0052 ,,	·85 ,,
	·0070 ,,	·82 ,,
	·0089 ,,	·80 ,,
Silver.	0·0 cm.	1·00 $\times x$
	·002 ,,	99 ,,
	·004 ,,	·99 ,,
	·006 ,,	1·00 ,,
	·012 ,,	·99 (5) ,,
Tin.	(1) 0·0 cm.	1·00 $\times x$
	(3) ·002 ,,	·98 ,,
	(9) ·002 ,,	·97 ,,
	(4) ·004 ,,	·99 ,,
	(5) ·004 ,,	·96 ,,
	(8) ·0058 ,,	1·00 ,,
	(6) ·0058 ,,	·95 ,,
	(2) ·01 ,,	·89 ,,
	(7) ·01 ,,	1·00 ,,

Thus when measured in silver and in some cases when measured in tin, the absorption of the scattered radiation was identical with that of the primary. This may be called unmodified scattering. But the same unmodified scattered radiation appeared as a modified scattered radiation when measured in paper, aluminium or copper, and modified to a smaller extent) when measured in tin and gold. Again, a natural criticism of the experimental results if they were of doubtful accuracy, might be that silver and tin are not so sensitive to a change of wave-length of a more or less heterogeneous beam because their K characteristic radiations have a wave-length within the range of these experiments, and thus the diminution of the L, M, N absorptions with increase of frequency might be roughly compensated by the appearance of the K absorption. A sufficient answer to that is that silver and tin *do show* the difference between primary and secondary when the critical condition is obtained in these substances, *i. e.* when a J-discontinuity in silver or tin is produced. It is perhaps unnecessary to show the results of such experiments; the truth is sufficiently clear for tin in fig. 2, though other experiments illustrate it with greater accuracy.

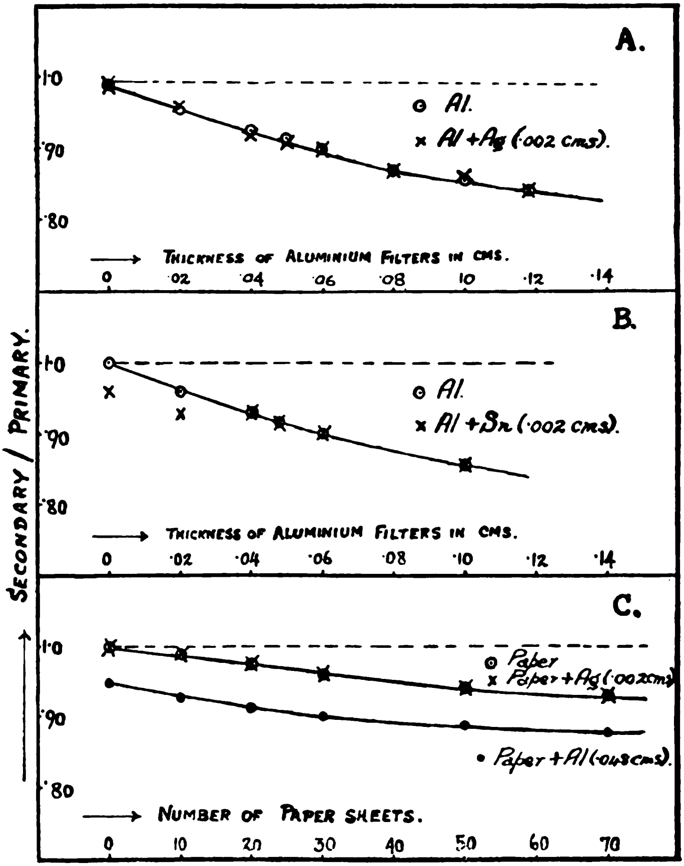
As the scattered radiation differs from the primary when measured in some substances, and not when measured in others, the question naturally arises, do substances of the former class when used to measure the absorbability *produce* the change—say of wave-length—in the secondary radiation and subsequently show that change? It appeared that such a transformation might possibly take place, for the J-discontinuity involving a change of absorption coefficient has been shown to be produced by mere filtering of a heterogeneous radiation. The answer to this question can be given if we can find any one substance which shows no difference between these scattered and primary radiations *subsequent to* these having been proved different when measured in other substances. In fig. 3 curves are shown giving the relation between S′/P′ and thickness of absorbing substance, firstly when that absorbing substance was alone, and secondly when accompanied by a sheet of a second absorbing substance which did not show the difference between primary and secondary.

Thus, curve A shows by circles the value of S′/P′ for various thicknesses of intercepting aluminium. The slope shows the intensity of the secondary to fall more rapidly than the primary. But when, in addition to the aluminium, sheets of silver (·002 cm. thick) were placed in both beams, the ratio S′/P′ was absolutely unchanged, as shown by the crosses. Transmission through silver produced no further change in the ratio of the secondary to primary,—that is they were equally absorbable in silver.

Curve B was obtained in precisely the same manner, but tin was used as the second absorbing substance. In this case the tin sheet definitely did absorb the scattered radiation more than the primary in two cases, as is shown by the two crosses below the circles. But in the other cases transmission through tin produced absolutely no change in the ratio of secondary to primary: crosses and circles are superposed. Thus, in agreement with previous experiments, tin showed the difference in some experiments and not in others, though they were all in the same series.

Fig. 3.

Showing that *after transmission* through substances Al and Paper which indicate a "modified scattered radiation" this is still "unmodified" to Ag and sometimes to Sn.



Exper. A. Filtering by Al (⊙); Al with Ag ·002 cm. (×).
„ B. „ „ (⊙); „ Sn ·002 cm. (×).
„ C. „ Paper (⊙); Paper with Ag ·002 cm. (×).
Paper with Al ·048 cm. (•).

Curve C shows by circles the ratio S′/P′ after transmission through paper of varying thickness; by crosses a similar ratio after passing through silver in addition to the paper; and by dots the corresponding ratios after transmission through aluminium in addition to the paper. The results show that after transmission through paper. which shows the difference between scattered and primary, the difference is also shown in aluminium, but is not indicated to the slightest extent in silver. Yet silver is quite capable of showing a difference when certain conditions are attained, as is indeed shown above in the case of tin.

Thus a change of absorbability of X-radiation by scattering is dependent on a relation between the radiation and the substance used to test those radiations. There is absolutely no difference in the absorbability when tested in some substances—even subsequent to transmission through those substances which exhibit a difference. How then can there be a wave-length change either in scattering or in the subsequent transmission of the scattered radiation through matter? Can wave-length depend upon the testing substance, or can even the evidence of a change of wave-length be shown so markedly in some substances and not at all in others?

Scattering at Various Angles.

According to Compton's theory of quantum-scattering of X-rays the change of wave-length produced by scattering is given by $\delta\lambda = \cdot 024(1-\cos\phi)$ Ångström units, and thus should vary with the angle of scattering ϕ. Again we have found no confirmation of this by the absorption method: what has been observed has been either absolutely no difference or a well-marked difference between the secondary radiations proceeding in two directions, and this difference is due to a definite step in the activity and absorbability such as is characteristic of the J phenomenon. Thus the variation with angle occurs only in steps, between which there is no variation at all.

Barkla and Miss Mackenzie[*] showed that when a difference between the two beams scattered at 60° and 120° with the direction of propagation of the primary did appear, it was in one of two forms (*a*) or (*b*). In case (*a*) the difference was not one of general absorbability, but was shown by sudden changes in the ionization produced by the beam at 120° when by absorption it reached certain absorbabilities, while the beam at 60° did not show these discontinuities. In case (*b*) the beam at 120° was continuously more absorbable than that at 60°. Case (*a*) obviously indicated no change of wave-length, for there was no difference in absorbability. Case (*b*) had the superficial appearance of a difference in wave length, but other experiments showed that the difference of absorbability was the precise difference involved in the change of level of the activity called the J-transformation, and was due simply to a difference in the properties of the two radiations depending on something quite different from wave-length. This something is a property of the beam as a whole and not of its constituent wave-lengths, except as they contribute to some kind of average for the whole stream of radiation.

---

[*] Phil. Mag. Feb. 1926.

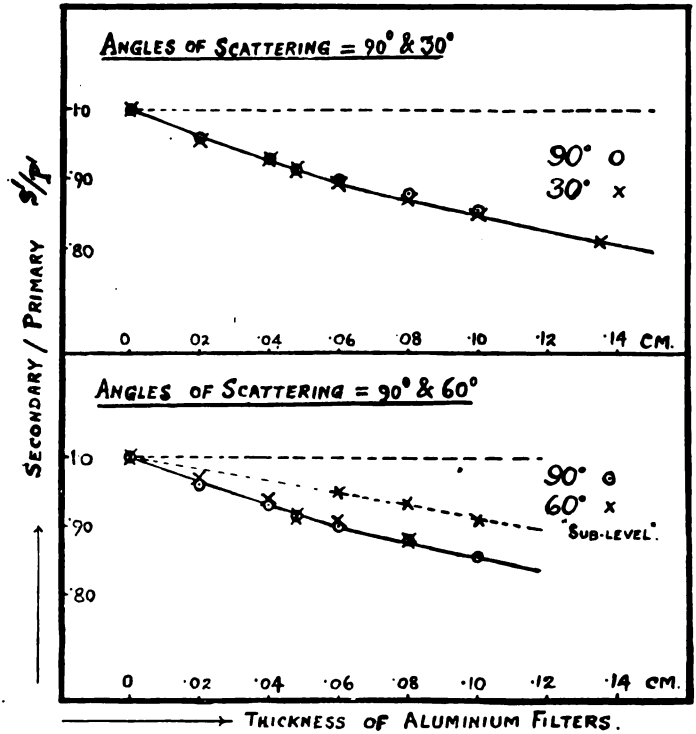
Instead of comparing the two scattered beams directly we have in these experiments compared the radiations scattered at various angles 30°, 60°, and 90° with the primary radiation producing them. This we did, as before, by placing equal thicknesses of absorbing aluminium in the path of both primary and secondary radiations. Briefly the results may be stated thus:—When the difference between the primary and secondary is observed, in general it has the same magnitude whatever the direction from which that secondary radiation proceeds, within the limits of J-discontinuities. Any variation with angle occurs in the familiar finite steps of the J-discontinuities. In the Barkla and Mackenzie experiments it was the scattered radiation at 120° which differed from the primary, while that at 60° was like the primary (or differed from it by a constant smaller amount).

Fig. 4 shows in its upper section the results of experiments by which the scattered radiations at 30° and 90° were compared with the primary radiation and with one another. As before, the ordinates are values of S'/P' for the various values of the thickness of aluminium intercepting both secondary and primary beams. The slope of the curve measures the difference between secondary and primary beams. The circles represent observations made upon the radiation scattered at 90°, while the crosses give the corresponding values for S'/P' when the scattered radiation experimented upon was at an angle of 30°. The almost perfect superposition of circles and crosses shows that while they both differed considerably from the primary, the two secondary beams had identical absorbabilities. In the lower section of fig. 4 a similar comparison is made between the radiations scattered at 60° and 90°. In this case again, the two scattered beams had identical absorbabilities in a number of measurements; whereas three other measurements showed the beam at 60° to be distinctly less absorbable than that at 90°. This change is of the kind that would be given by Compton's variation of wave-lengths with scattering angle.

It indicates, however, only a definite change of the level of activity of the radiation governed not by wave-length but by a quality of the whole radiation. The difference between the primary and scattered radiations is again shown for

Fig. 4.

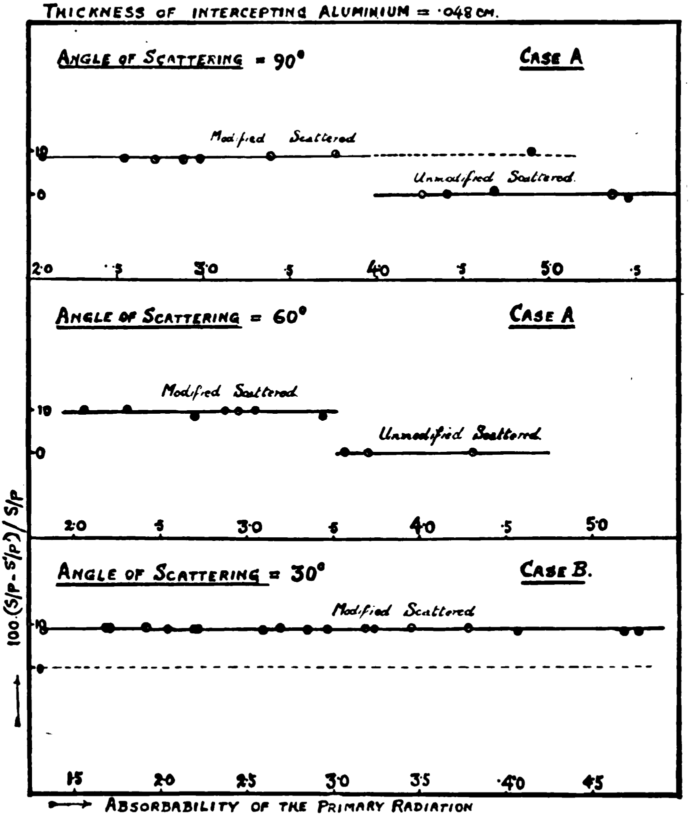
Comparing radiations scattered at different angles.



various angles of scattering in fig. 5. In this case the intercepting aluminium was of constant thickness while the wave-length of radiation varied. The difference is seen to be independent of the angle, *i. e.* the same for 30°, 60°, and 90°. The ordinates show the percentage change in the ratio S/P produced by transmission of both primary and secondary beams through ·048 cm. of aluminium (S′/P′). It will be observed that for soft radiations (the right-hand side of the figure) there was absolutely no difference between secondary and primary beams scattered at 90° and 60°, but at the more penetrating end the scattered radiation appeared markedly softer than the primary, the percentage change in the ratio S′/P′ being about 9 per cent. *whatever the original absorbability of the radiation and whatever the angle of scattering.* This corresponds to a constant difference of absorption coefficient between primary and scattered. [See previous paper.]

Fig. 5.

Showing the degree of "modification" to be independent of angle of scattering.



The difference between secondary and primary when it appeared at all was thus independent of the angle of scattering. (It would appear from the results shown in fig. 5 that when soft radiation was used the radiation scattered at 30° was more absorbable than that scattered at 60° and 90°.

These experiments were, however, made at different times, consequently with different radiations. A direct comparison at the same time, *i. e.* with a given primary radiation, has never shown the radiation scattered at the smaller angle to be more absorbable than that scattered at greater angle). Again, the phenomenon is simply an illustration of the J-transformation, *i. e.* a change in the level of the activity due to characteristics of the radiation other than wave-length.

It should be noted that Compton's theory indicates a very minute change of wave-length by scattering at 30°; for high frequencies at this angle our observed change in absorption is thirty times that calculated after Compton ; whereas for low frequencies *when no modification was observed* at 90° it was less than 1/10 (possibly 1/20) of what would be expected on the Compton theory. As previously indicated, there is close agreement when a modification does appear for wave-lengths in the neighbourhood of that of "Mo K" radiation and the scattering angle is 90°. But the agreement is accidental.

SUMMARY OF EXPERIMENTAL RESULTS.

The following results, which were obtained and confirmed in many experiments, are illustrated in the preceding paper:—

(1) When a heterogeneous X-radiation is scattered, the scattered radiation has either precisely the same absorbability as the primary, or there is a well-marked difference between the absorbabilities when measured in any one substance. (Shown in previous paper.)

(2) When the scattered radiation is different from the primary when measured in certain substances, its absorbability may be, and frequently is, precisely like that of the primary when measured in certain other substances.

(3) Even after transmission through substances which show the difference between primary and secondary radiations, there is still no difference between the two when measured in certain other substances.

(4) When the scattered radiation is observed in different directions making angles of 30°, 60°, and 90° with the primary beam, and when these radiations differ from the primary in their absorbability in a certain substance, they, in general, differ by precisely the same amount. When a difference appears with increasing angle of scattering, it takes place abruptly—by a jump.

DISCUSSION.

The above facts are all explained in terms of the J phenomenon—that there are different possible levels for the activity of a beam of X-rays, the particular level of activity being dependent not upon any constituent wave-length of the radiation, but upon a coherence of the whole radiation and upon the relation between the average constitution of the radiation (closely allied to temperature) and characteristic "temperatures" of the substance traversed.

Indeed, in all our investigations upon the scattered radiation, the difference which we have observed between it and the primary is a difference such as also appears through operations quite different from scattering. It is a difference due to properties of a coherent beam and may under suitable conditions be produced by slight filtering, or by the superposition of a feeble radiation upon the beam studied, or in other ways. *These* cannot be, or should not be, described as changes in wave-length.

On the other hand, we find absolutely no indication of Compton's wave-length change by scattering, and all the laws governing the change observed by us—the manner of its appearance, its magnitude, its variation with frequency and with the angle of scattering—appear entirely at variance with Compton's view.

All the apparent conflict of results may just possibly be due to the fact we have already established—that a considerable portion (at least) of the properties of an X-radiation is not fundamentally associated with the wave-length, but with this "temperature," measured to a certain degree of approximation by absorption-coefficient,—that Compton measures one property; we measure another, a more intimately related one; and that these two properties are not related in the way which experiments upon homogeneous radiations have indicated. But though a change in activity,—a change in properties,—is certainly brought about by methods which cannot involve a change in wave-length (but only a slight change of average wave-length or a change of "temperature" of the whole beam), the assumption that a change of wave-length of such magnitude as that of the Compton effect could occur without some corresponding marked change in the ionizing and penetrating properties of the radiation such as we could easily detect, is too revolutionary to accept without either experimental or theoretical justification. It would mean that the properties are practically independent of wave-length or frequency of the constituent radiations. Yet apart from that, there is no alternative to the conclusion that the Compton effect does not occur in our experiments on heterogeneous beams and without a diffracting crystal.

Besides that, in place of the Compton effect we observe the J-transformation, which though governed by different laws shows a remarkable correspondence with the Compton effect. The alternatives thus are:—

(1) No Compton effect in all our experiments, or
(2) A complete divorce of the activity of an X-radiation from wave-length, and the substitution of an entirely new system of laws.

Briefly then, we find that the difference between a scattered and a primary X-radiation is simply expressed by saying that the scattered radiation has characteristics of structure which make it much more favourable to the J phenomenon than is the primary radiation. The fact of *coherence* suggests a reason for this, for coherence implies a certain persistence (a continuity of action) such as might be produced by

(1) a scattered radiation when the primary radiation is too intermittent to cohere;
(2) a scattered radiation making a large angle with the primary when that making a small angle is not sufficiently homogeneous (on a large scale);
(3) a scattered radiation from a thick radiator when that from a thin radiator is not sufficiently homogeneous.

The hypothesis would also explain the apparently capricious nature of the J phenomenon, for the stream of X-radiation might be expected to be sufficiently continuous (sufficiently homogeneous) by some methods of excitation and not by others. Such a dependence on the details of excitation has been found (Barkla and Mackenzie, unpublished).

This explanation is as yet merely hypothetical and should be distinguished from the *fact of coherence* of the constituent radiations in a beam. Of this there can be no possible doubt. Quite outside the sphere of speculation is the fact that the ionization produced by a beam of X-rays is not dependent on

(1) simple wave-length and intensity on the one hand (classical theory),
or (2) independent quanta and the number of these on the other hand (quantum theory),
or (3) any combination of these;

but, in part at least, upon a quality of the full stream of radiation more closely allied to temperature. This is the meaning of the J phenomenon, and this forms the basis of the explanation of all we have observed in our comparison of the scattered and the primary X-radiations.

The J phenomenon will be further described and discussed in later papers.

LVIII. *The Compton Effect and the Reflexion of X-Rays by Crystals.* *By* E. J. Williams, *M.Sc., Fellow of the University of Wales* *.

§ 1. *Introduction.*

IT has been found by A. H. Compton that when X-radiation is scattered by matter the wave-length of part of the scattered radiation is longer than that of the incident radiation, the rest of the scattered radiation being unmodified. The bearing of this phenomenon on the diffraction of X-rays by crystals has, so far, received little attention †. In calculating the positions and intensities of the diffracted beams, it has been assumed that all the radiation scattered by the electrons in the crystal has the same wave-length as the incident radiation. It is found that the laws of reflexion derived on this supposition are obeyed by *all* the radiation reflected by a crystal, from which it follows that either (1) no modified radiation is reflected by a crystal, or (2) the modified radiation obeys the same laws of reflexion as the unmodified radiation to within the error of observation. Should (1) be correct, it is possible that we must modify the estimates of the intensity of reflexion based on the assumption that the scattered radiation in every respect obeys the classical laws. For the total amount of radiation scattered, including modified and unmodified, corresponds to the amount given by the classical theory, so that, if the electrons in the crystal scatter modified radiation which is not reflected, only part of this amount will be available for building up diffraction maxima. It is the purpose of this paper to examine these questions, and in particular to investigate the effect on the intensity of reflexion. The laws of reflexion of the modified radiation will first be considered in order to test the possibility of (2).

§ 2. *Laws of Reflexion of Modified Radiation.*

In order to consider a phenomenon of interference it is necessary in the present state of radiation theory to assume the wave theory. Furthermore, in order that a change of wave-length be intelligible on the wave theory it is necessary to suppose the scattering electrons to be moving, in which case a change in wave-length follows as a Doppler effect. A supposition of this nature was made by Compton[*] in considering the distribution and intensity of the modified radiation scattered by an amorphous substance. He showed that, if the scattering electrons travelled in the direction of the incident rays with a velocity $h/m\lambda$, the wave-length of the radiation scattered in any direction would be that required by the quantum theory of scattering. Compton showed that the calculated distribution obtained in this way is in substantial agreement with the observed distribution, and this result warrants the use of the same method in order to obtain the laws of reflexion of the modified radiation. The supposition made here is that the actual distribution of the diffracted beams is the same as that which, on the classical wave theory, would result from the scattering of the radiation by an electron lattice moving with the velocity $h/m\lambda$.

---

* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

† In a recently published paper (*Zeit. für Phys.* xxxvi. 2, 1926) Kellmann and Mark consider some aspects of the question, and reference will be made to their work in the parts concerned.

Let λ = wave-length of the incident X-radiation as measured by a stationary observer;

ox = direction of incident rays, so that the moving scatterers have a velocity $h/m\lambda$ parallel to ox.

Then for an observer moving with the scatterers the wave-length of the radiation before and after scattering is $\lambda(1+\beta)$ where $\beta=h/m\lambda c$, powers of β higher than the first being neglected. The angles of incidence and reflexion measured by this observer are given by Bragg's law, and we have

$$2d\sin\theta=n\lambda(1+\beta), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where θ is the common value of the angles of incidence and reflexion.

As the direction of motion is parallel to the incident rays the angle of incidence is the same for the two observers. The angle of incidence, ϕ_i, measured by the stationary observer is therefore given by

$$2d\sin\phi_i=n\lambda(1+\beta). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If ϕ_r denote the angle of reflexion, then $\phi_i+\phi_r$ is the angle between the reflected rays and the direction of relative motion measured by the stationary observer. The angle between the reflected rays and the direction of relative motion is 2θ for the moving observer, so that from the law of aberration[†]

$$\cos 2\theta=\cos(\phi_i+\phi_r)-\beta/1-\beta\cos(\phi_i+\phi_r). \quad . \quad (3)$$

---

[*] Phys. Rev. 2, xxi. (1923).

[†] *Vide*, e.g., O. W. Richardson, 'Electron Theory of Matter,' p. 306.

It follows from (1), (2), and (3), on neglecting higher powers of β, that

$$2d \sin \phi_r = n\lambda(1 - \beta + 2\beta \sin^2\alpha), \quad . \quad . \quad . \quad (4)$$

α denoting the angle of reflexion of the unmodified radiation. On substituting for β its numerical value, (2) and (4) become respectively

$$\left.\begin{aligned} 2d \sin \phi_i &= n(\lambda + {\cdot}024), \\ 2d \sin \phi_r &= n(\lambda - {\cdot}024 + {\cdot}048 \sin^2\alpha), \end{aligned}\right\} \quad . \quad . \quad . \quad (5)$$

d and λ being expressed in Ångström units.

The common value, α, of the angles of incidence and reflexion of the unmodified radiation is given by

$$2d \sin \alpha = n\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The laws of reflexion of the modified radiation (equation 5) are thus not the same as those of the unmodified radiation (equation 6) and, as will be shown presently, the difference between them is such that if the radiation scattered as modified radiation by a substance in the amorphous form was regularly reflected by a crystal of the substance according to (5) the phenomenon would have been detected experimentally. For such detection (1) the modified and unmodified beams must be resolvable; (2) the intensity of the modified beam must be sufficient.

The separation of the incident modified and unmodified rays corresponds to a wave-length interval of ·024 Å (*cf.* equations (5) and (6)), which is six times the difference between the Kα_1 and Kα_2 lines of rhodium. The rhodium Kα_1 and Kα_2 lines can, however, be resolved by a spectrometer of moderate resolving power, so that the modified beams certainly satisfy the condition of resolution.

In order to discuss the second condition we shall take the particular case of a rock-salt crystal and consider the reflexion from planes having the structure factor Na + Cl of order such that the glancing angle is about 30°. The angle of scattering will then be about 60° and the ratios of the energies of the modified and unmodified radiations scattered through this angle by amorphous Na and Cl are about 1 and ·5 respectively*. If the ratio of the energies of the reflected modified and unmodified beam was of this magnitude, *i. e.* ·5 to 1, the modified beam would be sufficiently intense to be easily observed *. The intensity of reflexion depends on the sizes of the orbits which the scattering electrons describe. The larger the orbit the less in general is the contribution to the intensity of reflexion, and as there are reasons to believe that the outer electrons are mostly responsible for the modified rays, it follows that the ratio of the intensity of the modified reflected beam to that of the unmodified beam would be less than the ratio of the intensity of the modified radiation to that of the unmodified radiation scattered through the same angle by the same substance in the amorphous form. This effect of the distribution of the two radiations between the various classes of electrons in the atom can, however, hardly affect the order of magnitude of the ratio, and as this is about unity it is practically certain that the modified radiation if reflected would be sufficient to produce a beam of detectable intensity. In all the observations which have been made on the reflexion of X-rays by crystals no radiation obeying a different law from (6) has been detected. It is concluded, therefore, that the second alternative mentioned in § 1 cannot be admitted, and we are led to the first which states that no modified radiation is reflected by a crystal †‡. The bearing of this result on the theory of the intensity of reflexion by crystals will now be considered.

---

* These values are computed from results of observations on neighbouring elements made by Compton, Ross, and others.

§ 3. *The Compton Effect and the Intensity of Reflexion.*

The conclusion arrived at in the last paragraph admits two alternatives :

(*a*) No modified radiation is scattered by the electrons in the directions of regular reflexion.

(*b*) Modified radiation is scattered by the electrons in the same way as if they belonged to amorphous material, but is not regularly reflected.

It would seem at first that the orderly arrangement of atoms, which characterizes crystals, ought not to influence the initial scattering by the individual electrons and that (*a*) could accordingly be dismissed. However, the phenomenon of reflexion from crystals is one in which the electrons cooperate in the scattering, and it may be possible that this cooperation means a big increase in the effective mass of the scattering electrons in so far as encounters between them and the incident quanta are concerned The change of wavelength, being inversely proportional to the mass of the scatterer, would consequently be much smaller than that which ordinarily characterizes the modified radiation. In other words, the modified radiation, when reflected, automatically becomes "unmodified," owing to the increase in the effective mass of the scattering electrons. If the "modified" radiation becomes sufficiently "unmodified" as to be able to interfere with the ordinary unmodified radiation, the classical theory of the intensity of reflexion needs no revision. It may be, however, that this is not so, in which case there is an effect on the intensity of reflexion. This possibility will not be discussed any further at present, and the effect on the intensity of reflexion will be considered on the basis of the second alternative (*b*).

---

* The $K\alpha_1$ line of rhodium possesses only a third of the energy of the $K\alpha_2$ line and is quite prominent, though separated from the $K\alpha_2$ line by a much smaller angle than that which would separate the modified $K\alpha_1$ line from the unmodified $K\alpha_1$ line.

† This conclusion depends of course on the validity of the method used to derive the laws of reflexion of the modified radiation.

‡ Kallmann and Mark (*loc. cit.* p. 134) have independently arrived at this conclusion by a process of reasoning essentially the same as that used here.

According to (*b*) the amplitudes of the modified and unmodified waves due to the individual electrons in the crystal are the same as they would be if the electrons belonged to amorphous material, and the amplitude of the reflected wave is the vector sum of the amplitudes of the unmodified waves *. The intensity of reflexion will evidently be different from what it would be if all the scattered radiation was capable of being reflected, and the effect will now be considered mose in detail.

---

* The number of unmodified quanta that leave a crystal in the direction of reflexion is considerably greater than the number that would leave an amorphous body in that direction. The radiation scattered by an amorphous body is symmetrically distributed about the forward direction so that the momentum communicated to the body from the radiation is in this direction. In terms of the quantum theory this means that the directions of recoil of the scatterers are symmetrically distributed about the forward direction. In the case of reflexion by a crystal, the resultant momentum imparted to the crystal as the result of scattering is not in the forward direction but has a component perpendicular to the reflecting planes as well as a forward component. On the quantum theory this means that there is a preponderance of scattering bodies which recoil with components normal to the reflecting planes (on the side remote from the incident and reflected beams). In view of this we must suppose that the reinforcement of the scattered waves in the direction of reflexion influences the encounters between the quanta and electrons in such a way that a preponderance of quanta leave the electrons in the direction of reflexion, and the dynamical conditions of such encounters may be supposed to be the same as those holding in the case of the much lesser number of unmodified quanta that would be scattered in the same direction were the substance amorphous. This influence must not be confused with that discussed in connexion with (*a*). The supposition made there is that the reinforcement giving rise to regular reflexion increases the effective masses of the electrons.

The formula for the intensity of X-ray reflexion involves quantities, F, which represent the ratios of the amplitude of the wave scattered by an atom as a whole to that of the wave scattered according to the classical theory by a single electron. These are the quantities the estimated values of which have to be revised in order to allow for the non-reflexion of the modified radiation *. The revised values, which we shall denote by F_u, represent the ratio of the amplitude of the unmodified wave scattered by an atom to the amplitude of the wave which a single electron would scatter according to the classical theory, and these values have been calculated for the atoms of certain elements.

A calculation of F_u requires a knowledge of the relative amounts of the modified and unmodified scattered radiations respectively †. G. E. M. Jauncey ‡ has developed a quantitative theory of this partition of energy in the case of scattering by amorphous substances. The theory is based on the criterion, first suggested by A. H. Compton, that if a quantum does not give sufficient energy to the electron which scatters it to enable the electron to leave the atom, the quantum is unmodified.

It should be mentioned, however, that the general nature of the differences between the revised F curves and the classical curves can be deduced directly from the results of observations on the relative intensities of the modified and unmodified radiations scattered by different elements in the amorphous form, and the correction for the Compton effect is to this extent independent of Jauncey's theory.

Jauncey's theory refers to, and all observations have been made on, the *energies* of the two types of scattered radiation, whilst the quantity which is directly concerned in interference phenomena is the amplitude of the radiation. Let us consider a single electron and let j be the fraction of the energy scattered in a given direction which is unmodified, leaving a fraction $1-j$ of modified radiation. Now the coefficient of total scattering (including the modified and unmodified radiations) from light elements in the amorphous form, in which case the electrons scatter independently, obeys the classical theory *. Therefore, if the energy of the scattered radiation from a single electron according to the classical theory be denoted by unity, the absolute values of the energies of the unmodified and modified radiations are j and $1-j$ respectively. The energy of radiation is proportional to the square of the amplitude, and taking the constant of proportionality as unity the amplitude of waves scattered according to classical theory will be unity. Actually there are two trains of scattered waves representing energies j and $1-j$ respectively. In deducing the relation between the energies and amplitude there are two alternative suppositions which can be made and which lead to slightly different results. We can suppose that the electron is simultaneously scattering the two types of radiation having relative energies in the ratio of j to $1-j$, or alternatively, that the two radiations are scattered intermittently, the aggregate times being in the ratio of j to $1-j$. On the first assumption the amplitudes of the unmodified and modified waves scattered by a single electron are $\sqrt{j}$ and $\sqrt{1-j}$ respectively. According to the second, unmodified waves of unit amplitude will be scattered for a fraction j of the time and modified waves of unit amplitude for a fraction $1-j$ of the time, and as far as reflexion is concerned this state of affairs is equivalent to simultaneous scattering in which the amplitudes of the unmodified and modified waves are j and $1-j$ respectively. Revised values (F_u) of F have been calculated on the basis of each of the two suppositions. The value of F_u obtained on the first supposition will be denoted by F_{u_1}, and that on the second supposition by F_{u_2}.

---

* The values of F according to the classical theory have been calculated by D. R. Hartree, Phil. Mag. vol. l. p. 289.

† The allowance for the Compton effect cannot be made directly from a knowledge of the fraction of the radiation that is unmodified when the substance is in the amorphous form. The relative amounts of unmodified and modified radiations are different for electrons belonging to different orbits, and as the diffraction effect is also different for the different orbits it is obvious that the correction has to be made separately for the various orbits.

‡ Phys. Rev. (2) xxv. pp. 314, 723 (1925).

The value of j according to Jauncey's theory depends on the ionization energy of the electron, the magnitude and direction of its orbital velocity, the wave-length of the X-rays, and the glancing angle, β. The dependence on the last two quantities is a function of $\sin\beta/\lambda$, so that β and λ are not involved separately. If B^2 and ϵ denote the orbital kinetic energy and ionization energy respectively of an electron for which all directions of motion are equally likely, then j is given by

$$j = \cdot 5 + \epsilon/4B\psi - \psi/4B, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $\psi = 2h/mc \times (\sin\beta/\lambda)$.

---

* This applies to neither of the two radiations separately, the relative intensities of the modified and unmodified radiations varying considerably with wave-length and angle of scattering.

The value of j will be different for different orbits, and in the case of non-circular orbits will be different for different parts of the orbit[*]. The same applies to the diffraction effect and in calculating the values of F_u the different orbits in the atom have been considered separately, and in the case of non-circular orbits the different elements of the same orbit. Hartree[†] shows, in a paper on "The Atomic Structure Factor in Crystal Reflexion," how to calculate the values of F on the classical theory. In calculating the revised values considerable use has been made of tables given in this paper. Data relating to the potential field of certain atoms have also been kindly given to the writer by Mr. Hartree.

§ 4. *Discussion of "F" Curves.*

The values of F_c[‡], F_u and F_{u_2} for different values of the glancing angle β, for the calcium ion (Ca^{++}) and the fluorine ion (F^-) are given in Table I., the values of $\sin\beta$ corresponding to the wave-length Rh.Kα rays ($\lambda = \cdot 614$ Å.). Stoner's distribution of electrons has been assumed.

TABLE I.

Sin β ($\lambda = \cdot 614$ Å).	Ca^{++}			F^-		
	F_c.	F_{u_1}.	F_{u_2}.	F_c.	F_{u_1}.	F_{u_2}.
0·00	18	18	18	10	10	10
0·10	15·6	14·4	13·3	8·4	6·9	5·7
0·20	11·1	10·0	9·1	5·2	3·2	2·5
0·30	8·5	8·0	7·0	2·7	2·0	1·8
0·40	8·4	6·9	5·7	1·2	1·7	1·4
0·50	7·8	5·8	4·7	·6	1·5	1·2
0·60	6·3	4·9	3·9	1·0	1·3	1·0
0·70	5·0	3·9	5·1	1·8	1·1	·80

The results are shown graphically in fig. 1 together with curves which represent the observed values of F deduced from the actual intensity of reflexion by James and Randall *, using the reflexion formula. These curves will now be compared.

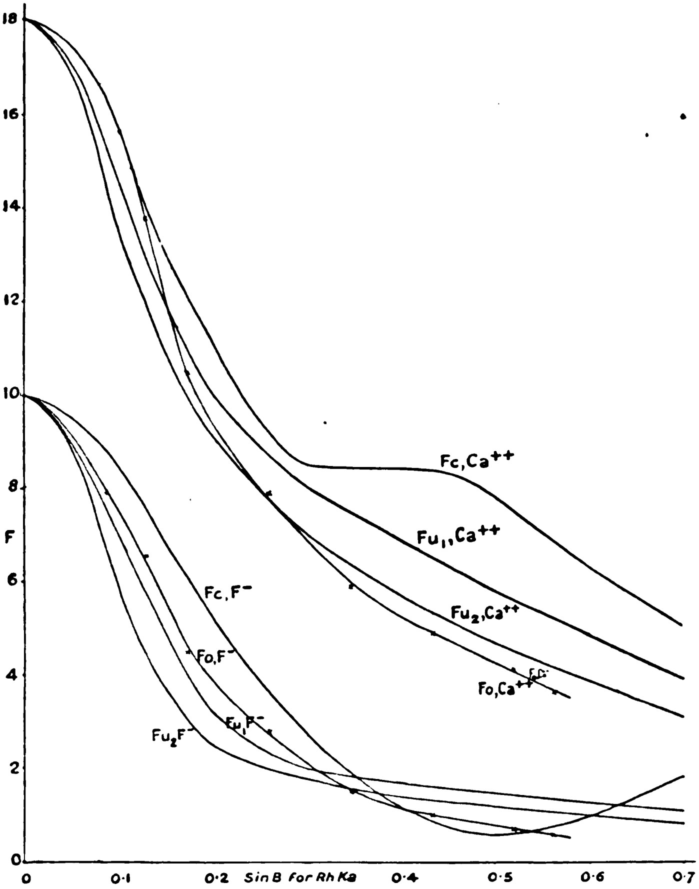
---

[*] In so far as the calculation of F is concerned, a circular orbit is equivalent to a spherical shell of electricity, and the effective value of j may be different for different parts of the same shell, being equal at any point to the value given by Jauncey's theory for an electron confined to move in the plane tangential to the sphere at that point. Such a possibility has not been allowed for in the present calculations, as an allowance for it would have little effect on the numerical results, there being in fact no effect when j for the whole orbit has the values 0, ·5, and 1.

[†] *Loc. cit.*

[‡] The values of F_c for Ca^{++} are taken from Hartree's paper (*loc. cit.*), and those for F^- have been calculated by Hartree's method.

Fig. 1.



i. *Order of magnitude of difference between the Curves.*

The difference between the F_c and F_u curves is quite appreciable in certain regions, the maximum difference between the values of F_c and F_{u_1} in the case of calcium, for instance, being about 25 per cent., whilst the values of F_{u_1} for fluorine are in some places only half those of F_c and in other places are twice those values. The difference between F_c and F_{u_2} is still greater but is everywhere in the same direction, the curves F_{u_1} and F_{u_2} being very similar. The revision of the values of F has, however, not produced a radical departure from the classical values. Had the revision resulted in such a difference there could not be any agreement between the revised values and the observed values.

---

* James and Randall, Phil. Mag., May 1926.

ii. *Initial Values.*

The values of F_c and F_u are seen to be the same at zero glancing angle, being equal to the number of electrons in the ion. It can be readily seen why this should be the case. For when the angle of scattering is zero the momentum communicated to the scattering electron is zero and the electron cannot possibly be ejected from the atom. As this is the condition for modification, it follows that all the radiation scattered in the forward direction is unmodified, and consequently the values of F_u and F_c are the same.

This result is not entirely dependent on Jauncey's theory, but can be deduced in a general way from the observed intensities of the unmodified and modified radiations. These show that the relative intensity of the modified radiation falls off quickly with decreasing angle of scattering and would indicate that at zero glancing angle there would be no modified radiation scattered, thus making $F_u=F_c$ as above.

The actual values of F at zero glancing angle or extremely small glancing angles cannot of course be obtained from observations on the intensity of reflexion, as there are no reflexions at glancing angles less than about $\sin^{-1}.1$. As a result of determinations of the absolute values of F for Na and Cl at this and bigger angles, Bragg, James, and Bosanquet[*] concluded, however, that "the values for F when $\sin\beta=0{\cdot}1$ are of the order to be expected if the curves for chlorine and sodium have maxima at about 18 and 10 respectively." These numbers are the theoretical maximum values of F, being the respective numbers of electrons in the two ions.

In the determination of the "observed" values of F for Ca and F, James and Randall[†] chose a value of the extinction coefficient which made the observed value for Ca at $\sin\beta=0{\cdot}1$ coincide with the value calculated by Hartree on the classical theory. These authors show that the value for the extinction obtained in this way leads to consistent results when intensities of reflexion for planes with structure amplitudes $Ca+F_2$, Ca, $Ca-F_2$, are compared, thus showing that the value must be nearly correct. In comparing the F curves in fig. 1 it must, therefore, be realized that James and Randall have made F_c and F_o coincide at the smallest glancing angle at which reflexion is observed, and that the better agreement between F_c and F_o than between F_{u_1} or F_{u_2} and F_o for small angles is not necessarily real.

---

[*] W. L. Bragg, R. W. James, and C. H. Bosanquet, Phil. Mag. (6) xli. p. 334.

[†] *Loc. cit.*

iii. *Flattening of* F *curve for* Ca^{++} *in region of* $\sin\beta = \cdot 35$, *and Rise in* F *curve for* F^- *after* $\sin\beta = \cdot 5$.

The classical F curves do not fall off uniformly with increasing glancing angle over the whole range under consideration, and in this respect differ from the observed curves and the revised curves. In the case of calcium there is a distinct sudden flattening of the F_c curve in the region around $\sin\beta = \cdot 35$, and in the case of fluorine the F_c curve begins to rise after $\sin\beta = \cdot 5$. The reasons for the presence of these characteristics in the F_c curves and their absence in the revised curves can be made clear in a general way as follows.

The contribution from the outer orbits 3_1 and 3_2 in the case of $calcium^{++}$ falls off very rapidly with $\sin\beta$ and then oscillates in value, passing through a negative minimum value at $\sin\beta = \cdot 33$, and a positive maximum at $\sin\beta = \cdot 48$. In the case of fluorine the contribution to F from the outer orbits 2_1 and 2_2 reaches a minimum value at $\sin\beta = \cdot 5$ and then rises again. This oscillation is due to the relatively large sizes of the outer orbits and is absent in the contributions from the inner electrons in the region of glancing angles considered. This oscillating nature of the contribution from the outer electrons is directly responsible for the flattening of the F_c curve for calcium at $\sin\beta = \cdot 35$ and the rise in the F curve for fluorine after $\sin\beta = \cdot 5$. Now when we come to consider the values of F_u, we find that as the outer electrons are also more loosely bound the amount of unmodified radiation scattered by them falls off rapidly with increasing glancing angle, with the result that the contribution to F_u from these electrons is small, and does not affect the uniform falling off of the F_u curve for the whole atom *. This result is not wholly dependent on

---

* In fact the contribution that these electrons do give to F comes from the parts of the orbits close to the nucleus, and therefore possesses none of the characteristics resulting from large radial distances from the nucleus.

Jauncey's theory. The results of observations on the relative intensities of the modified and unmodified radiations scattered from elements of different atomic numbers show that the more loosely bound the electrons are to the atom the less unmodified radiation they scatter, and therefore the contributions to F from outer electrons must be relatively unimportant.

The above argument applies to all atoms and we can state, as a general result, that the classical F curve for an ion does not fall off uniformly with increasing glancing angle owing to the oscillating nature of the contributions from the outer electrons. In the case of moderately heavy atoms, such as Cl, K, and Ca, there is a distinct flattening of the F_c curve when F is about half its maximum value, and for light atoms, such as O and F, the curve passes through a minimum and then rises. On the other hand, the F_u curves for these atoms fall off uniformly because the contribution to F_u from the outer electrons is negligible in the region of glancing angles concerned. There is no evidence of these characteristics in the "observed" curves, and in this respect the agreement between the revised F curves and the observed curves is much better than that between the classical F curves and the observed curves.

iv. *Values of* F *at relatively large angles.*

The "observed" values of F are not corrected for the Debye temperature effect. This effect is almost negligible at small glancing angles and becomes appreciable only at large glancing angles. The correction would somewhat increase the "observed" values at large angles and would improve the agreement between them and the values of F_u.

v. *Dependence of correction for the Compton Effect on wave-length and glancing angle.*

It has already been pointed out that the relative amplitudes of the modified and unmodified radiations do not depend on β and λ separately but are functions of $\sin\beta/\lambda$. This is so because the criterion for scattering with or without modification involves β and λ only in so far as they control the momentum imparted to the scattering electron, which is represented by $2hc \times (\sin\beta/\lambda)$. It is interesting to note that the correction for the Compton effect thus resembles other factors which determine the values of F, and that a curve in which F is plotted against $\sin\beta/\lambda$ will hold for all wave-lengths.

§5. *Power of a Crystal to reflect the modified and unmodified radiations scattered by its electrons.*

According to the prevailing theories of the Compton effect (due to Jauncey [*], Bohr, Kramers, and Slater [†]) there is no fundamental difference between the production of the modified scattered radiation and that of the unmodified scattered radiation. The difference is incidental and depends on whether the scattered quantum gives sufficient energy to the scattering electron to enable it to leave the atom or not. Certain experimental facts also add conviction to this view. The relative intensities of the modified and unmodified scattered radiations vary considerably with wave-length and scattering angle [‡]. Nevertheless, the magnitude of the coefficient of *total* scattering is independent of the wave-length over a large range, and the variation of the intensity of *total* scattering with scattering angle obeys the simple "$1+\cos^2\theta$" law. It follows that a decrease in the intensity of one type of radiation is always accompanied by a balancing increase in the intensity of the other. The two radiations are thus intimately dependent on one another, and hence cannot be produced by two fundamentally different processes. The reason for a state of affairs as described in § 3 (*b*) must therefore be found in minor differences between the two types of radiation. According to the above theories the "unmodified" scattered radiation is strictly speaking modified, the change of wave-length being, however, very small compared with that experienced by the "modified" radiation. The change in frequency of a quantum due to scattering is inversely proportional to the mass of the scattering body, and the theoretical change in the "unmodified" radiation, which on these theories is the result of encounters between quanta and atoms, is too small to be detected, being of the order of 10^{-6} Å. Nevertheless there is on these theories a change, and the difference between the modified and unmodified scattered radiations must be regarded as one of degree only. The question is whether this difference in degree can account for the non-reflexion of the modified radiation. In order to consider this question it is necessary, as it was in the discussion of the laws of reflexion of the modified radiation, to use the wave theory and assume hypothetical scatterers moving in such a way as to give the necessary change in wave-length. Compton[*] showed that the change in wave-length of the modified radiation follows as a Doppler effect if we assume the scattering electrons to be moving in the direction of the incident rays with a velocity $h/m\lambda$. In calculating the change in wave-length required by the quantum theory of scattering, Compton did not take into account the motion of the scattering electrons in their orbits. Jauncey subsequently extended the theory so as to take into account this motion, and showed that the change of frequency of the scattered quantum depends on the magnitude and direction of the velocity of the scattering electron at the instant of scattering, the change in wave-length being given by

---

[*] *Loc. cit.*

[†] Bohr, Kramers, & Slater, Phil. Mag. [6] xlvii., 1924.

[‡] The number of recoil tracks produced in oxygen, for instance, shows that at least 80 per cent. of the scattered radiation ($\lambda = {\cdot}61$ Å) is modified, whilst the spectrum of the radiation scattered by graphite through small angles shows a predominance of unmodified radiation.

$$\delta\lambda/\lambda = 2h\sin^2\theta/2/mc\lambda + 2u\sin\theta/2\,.\cos\phi/c, \quad . \quad (8)$$

where u is the magnitude of the orbital velocity of scattering electron and ϕ is the angle it makes with the momentum lost by the quantum. It follows from (8) that a single wave-length primary radiation should be scattered as a "band," different changes of wave-length being due to different values of ϕ and u. This is in accordance with observations, and Jauncey has shown that the extent of the observed "broadening" of the modified line is also quantitatively in agreement with the theory. In view of this effect it is not correct to assume a uniform drift of the hypothetical scatterers. These scatterers must be assumed to be moving with various different velocities, the range of velocities corresponding to the range of wave-lengths in the modified radiation. There are two hypotheses which can be made as regards this motion. We can associate a hypothetical scatterer with each electron in the crystal, the velocity of the hypothetical scatterer at any instant being that which would give the change of wave-length required by (1), u and ϕ referring to the corresponding electrons at that instant, or, we can regard the hypothetical scatterers as belonging to a multitude of classes, all the scatterers in the same class moving with the same velocity and therefore maintaining fixed relative positions. The first of these hypotheses will be made the basis of the present argument.

Let the vector w_0 be the velocity which gives a Doppler change of wave-length equal to that represented by the first term in (8), and let w be the velocity which gives a change of wave-length represented by the second term. Then a velocity w_0+w will give the complete change of wave-length required by (8). w_0 is the same for all the electrons concerned, so that the relative positions of the scatterers are not affected by this component of the velocity. The value of w, however, depends on u and ϕ, which continually vary as an electron moves in its orbit, so that u and ϕ at any instant may be different even for electrons describing similar orbits, and therefore w at any instant is different for the different hypothetical scatterers. Now if at any time, t_0, we suppose the relative positions of the scatterers to be the same as those of the electrons in the crystal to which they correspond, this will not be the case at any subsequent instant because of the variation in w. The component w_0, as already mentioned, does not affect the relative positions and can be left out of account. The important quantity is $\int_{t_0}^{t} w\,dt$ which represents the distance, at time t, of a scatterer from its mean position *. The same argument as the foregoing applies to the unmodified radiation, the only difference being that instead of (8) we have a similar equation with the mass of the atom and its velocity of thermal agitation, instead of the mass of the electron and its orbital velocity respectively. The velocity of the hypothetical scatterers associated with electrons which scatter unmodified quanta can then be represented by W_0+W, where W_0 is constant and W variable, and their displacement from their mean positions is given by $\int^t W\,dt$. We have now two systems of scatterers, the one moving with a uniform velocity w_0, its individual scatterers being at any instant at a distance $\int^t w\,dt$ from their mean positions; the other moving with uniform velocity W_0, the instantaneous displacement of its scatterers from their mean positions being $\int^t W\,dt$. The first system scatters modified radiation, the second unmodified radiation. Now, let us suppose that the value of $\int_0^t w\,dt$ is large compared with the wave-length, λ, of the X-rays, and that $\int_0^t W\,dt$ is small compared with λ. Then, in the first case the magnitude of the oscillation of the scatterers about their mean

---

[*] *Loc. cit.*

---

* If $\underset{t\to\infty}{\mathrm{Lt}}\left(\int_0^t w\,dt\right)/t$ is not zero (and equal to w_0' say), then $\int^t w\,dt$ does not represent the distance from the mean positions and it must be replaced by $\int_0^t (w-w_0')\,dt$.

position will reduce the amount of regular reflexion to a negligible value and no modified radiation is reflected, whilst in the second case it only causes a small decrease in the intensity of the reflexion so that the unmodified radiation is still reflected. In the present state of theory it is impossible to calculate the values of $\int W\,dt$ and $\int w\,dt$ without making several and very arbitrary assumptions, and such a calculation will not be attempted here. This discussion has, however, indicated a plausible way of accounting for the state of affairs represented by § 3 (*b*).

Summary.

The laws which would apply to the reflexion by a crystal of modified radiation scattered by its own electrons are derived by considering an electron lattice moving with a velocity that would give as a Doppler effect the change in wave-length demanded by the quantum theory of scattering. The difference between these and the ordinary Bragg laws of reflexion is appreciable, and as all the radiation actually reflected obeys Bragg's law it is concluded that (*a*) no modified radiation is scattered by the electrons in the directions concerned, or (*b*) modified radiation is scattered but is not regularly reflected. The bearing of the Compton effect on the theory of the intensity of reflexion by crystals is considered on the basis of the second alternative, and an outline of the way in which revised "F-curves" have been calculated is given. The "classical" F-curves, the revised curves, and the "observed" curves are compared. The revised F-curves are little influenced by the contribution from the outer electrons because these electrons scatter very little unmodified radiation, and as a result they agree much better than the classical curves with the curves actually observed. The correction for the Compton effect is a function of $\sin\beta/\lambda$, and in this respect resembles other factors entering into the theory of the intensity of reflexion.

The capacity of a crystal to reflect modified and unmodified radiation is discussed. There is no fundamental difference between the modified and unmodified radiations, and reasons for the incapacity of a crystal to reflect the modified radiation scattered by its electrons (if that is the case) must be based on minor differences between the two.

In conclusion I wish to thank Professor W. L. Bragg, F.R.S., for bringing the subject of the present investigation to my notice and for the kind interest which he has taken in the work.

APPENDIX.

The contribution to the value of F_u for the calcium ion from the electrons belonging to the 2_2 orbit will be considered in order to illustrate the way in which the revised values of F have been calculated. Hartree has shown that a circular orbit is equivalent, as far as the diffraction effect is concerned, to a spherical shell of electricity of radius equal to that of the orbit, and if all the radiation scattered was unmodified the contribution to F_u for each electron describing an orbit of this type would be that corresponding to a single stationary electron multiplied by the factor $\int_{-a}^{+a} \cos(4\pi x \sin\beta/\lambda)\frac{dx}{2a}$, which we shall denote by $C(\beta)$. The radius of the 2_2 orbit of calcium according to Hartree's formula (*loc cit.* p. 299) is ·134 Å, and the values of $C(\beta)$ for different values of the glancing angle, β, are given in the second column of the accompanying table. All the radiation scattered is, however, not unmodified, and the effective amplitude of the unmodified wave scattered by an electron is less than unity, being equal to j or $\sqrt{j}$ according to the supposition made as regards the nature of the scattering, j being the fraction of the scattered *energy* in the unmodified rays. In the present calculations j has been taken constant over the equivalent spherical shell, having a value equal to that given by Jauncey's theory for the whole orbit (equation 7). The value of j depends on the binding energy and orbital kinetic energy of the electron as well as on the wave-length and scattering angle of the rays. The values of the binding energy and orbital kinetic energy of electrons belonging to the 2_2 orbit

TABLE II.

Contribution to F_u for Calcium from electrons belonging to the 2_2 orbit.

Sin β.	$C(\beta)$.	j.	$\sqrt{j}$.	$6\times C(\beta)\times j$.	$6\times C(\beta)\times\sqrt{j}$.	$6\times C(\beta)$.
0	1·00	1·00	1·00	6·00	6·00	6·00
·1	·98	1·00	1·00	5·88	5·68	5·88
·2	·95	·84	·92	4·74	5·22	5·70
·3	·89	·67	·82	3·54	4·38	5·34
·4	·81	·57	·75	2·76	3·66	4·86
·5	·70	·50	·71	2·10	3·00	4·20
·6	·61	·44	·66	1·62	2·40	3·66
·7	·47	·39	·62	1·08	1·74	2·82

of a calcium atom are approximately 400 and 1000 volts respectively (computed from values given by Hartree for atoms of neighbouring elements), and the values of j or $\sqrt{j}$ are given in columns (3) and (4) of the table. In order to obtain the contribution to F_u the amplitude of the unmodified wave leaving the electron must be multiplied by the diffraction factor, $C(\beta)$. According to Stoner there are six electrons describing 2_2 orbits in the calcium atom, and the contribution δF_u to F_u from this class of electrons is therefore $6jC(\beta)$ or $6\sqrt{j}C(\beta)$, according to the supposition made as regards the nature of the scattering. The values of δF_u are given in the fifth and sixth columns. The contributions to F on the classical theory are given in the last column for comparison.

In the case of elliptic orbits different elements of the orbit defined by the distance of the electron from the nucleus have been considered separately, the calculation for each element being similar to that for a circular orbit. The value of F_u for the whole ion is obtained by adding up the contributions, δF_u, from the various classes of electrons in the ion.

LIX. *Radiation produced by the Passage of Electricity through Gases.* *By* Sir J. J. Thomson, *O.M.*, *F.R.S.*[*]

In the Philosophical Magazine for May 1925 I gave an account of experiments which showed that the passage of the electric discharge through gases at low pressures gives rise to the emission of radiations which, like radiation in the extreme ultra-violet or very soft X-rays, are absorbed with such rapidity that they cannot penetrate more than a thin layer of gas unless the pressure is very low; as they give rise to very intense ionization, they are of fundamental importance in the theory of the electric discharge through gases. In this paper I describe a series of experiments on the sources and characteristic properties of these radiations.

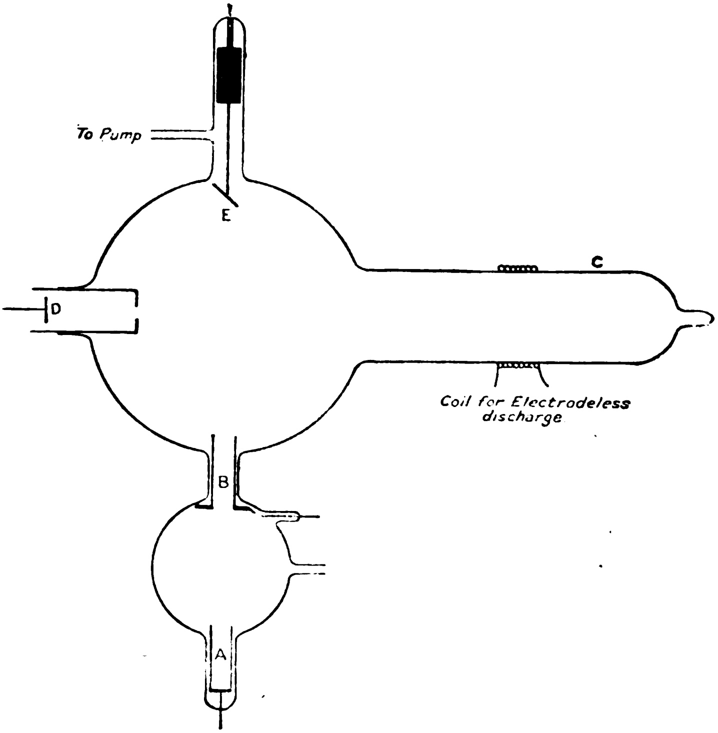
The experiments described in the earlier paper were made on the radiation coming from the space between the anode and cathode of a discharge-tube; in this region there are both moving electrons and moving positive ions, and their radiations are superposed. In the following experiments the effects due to the electrons and the positive ions were studied separately. For this purpose streams of either cathode or positive rays were isolated and sent past the window through which the radiations passed to the apparatus by which they were detected and tested.

---

[*] Communicated by the Author.

The electrodes A and B (fig. 1) for the discharge were placed at one end of a long tube. B is a brass or aluminium cylinder fitting tightly into the glass tube; a hole is bored out along the axis of this cylinder. A was in some cases a plane disk with its plane at right angles to the axis of B; in other cases it was a tube whose axis was in the same straight line as the axis of B. When A is made cathode a beam of cathode rays, and when it is made anode a beam of positive rays, streams through the boring in the cylinder B and excites radiation in the gas. This radiation is detected by the photoelectric effect it produces when it falls upon a polished metal disk D which is connected with a Dolezalek electrometer. In order to screen off from the disk the effects which would be produced by ions diffusing from the discharge-tube two methods have been employed, which

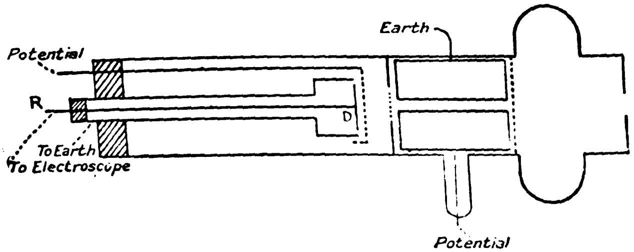
Fig. 1



are described on pp. 769 and 762, Phil. Mag. xlix. (1925). In the first of these methods the ions are stopped by a strong electric field and the radiation has not to pass through any solid obstacle, but passes through a slit between two half-cylinders insulated from each other and connected with the terminals of a battery of storage cells ; there is thus a strong electric field across the slit. The geometry of the apparatus was such that the beam of rays was parallel to the slit and was in full view of the disk D. The details of the electrical connexions and the position of screens of wire gauze to screen off any electrostatic effects due to the charges on the half-cylinders are indicated in fig. 2.

The efficiency of the screen for stopping the ions and electrons coming from the discharge was tested by increasing the potential difference between the half-cylinders. With the potentials used this increase produced no change in the deflexion of the electrometer, nor was any difference produced by reversing the direction of the field between the slits.

Fig. 2.



The other method used to screen off the ions is to place the disk D in a brass tube with a very thin celluloid window at one end ; the celluloid stops the ions, but allows some of the radiation to get through. I showed in the previous paper that even the thinnest celluloid obtainable stops all but a small fraction of the soft radiation coming from the tube.

Special precautions were taken to isolate the radiation coming from the molecules of the gas from that due to the impact of the electrons or positive rays against the walls of the discharge-tube. A side tube C (fig. 1) about 20 cm. long and 5 in diameter was used on to the main tube opposite to the testing apparatus, and the slit between the cylinders used to produce the screening electric field stopped down until the only part of the glass of the tube visible from the photoelectric disk was that at the far end of the tube C, which is far out of the path of the electrons.

The intensity of the stream of cathode or positive rays is estimated by the charge they give to the disk E (fig. 1), which is connected to earth through a high-resistance galvanometer. The disk can be moved backwards and forwards down the tube and can be brought within view of the disk connected with the electrometer ; when in this position the radiation due to the impact of the rays against the disk E, as well as that coming from the molecules of the gas, falls upon the testing apparatus, and by comparing the effects when E is in this position with those when it is pushed back we can estimate the relative intensities of these radiations.

Radiation due to the passage of cathode rays through the gas.

When the electrode A (fig. 1) was the cathode and a stream of cathode rays went through the opening in B past the window leading to the testing apparatus, the electrometer received a continuously increasing positive charge; this we ascribe to the ejection of electrons from the disk connected with the electrometer, due to the incidence of the radiation excited by the cathode rays in their course through the gas. If the stream of cathode rays is deflected by a magnet so that it can no longer be seen from the disk connected with the electrometer, the deflexion of the electrometer ceases, showing that the radiation came from the gas traversed by the beam of cathode rays and not from the walls of the tube.

If the target E is moved down the tube until it comes within sight of the disk connected with the electrometer so that the radiation excited by the incidence of the cathode rays on the metal target falls upon the disk, the deflexion of the electrometer is increased greatly, sometimes more than a hundredfold.

Radiation excited by positive rays.

When A (fig. 1) is made anode a beam of positive rays passes through the gas in sight of the disk connected with the electrometer, the electrometer acquires a continuously increasing charge of positive electricity, showing that the passage of positive rays through the gas excites radiation. In fact, when the electric discharge is produced by an induction coil the deflexion of the electrometer is greater when the induction coil is arranged to send a beam of positive rays through the tube than when the coil is reversed, so that cathode rays pass in front of the window. The number of positive and cathode rays passing past the window in unit time can be ascertained from the deflexions of the galvanometer which connects the target E (fig. 1) with the earth. Knowing the number of rays and the deflexion of the electrometer, we can calculate the deflexion due to one cathode or one positive ray. The result depends upon the nature of the screen used. When the ions are screened off by the electric field, the deflexion due to one positive ray is greater than that due to one cathode ray; when they are screened off by a celluloid film, the deflexion due to a cathode ray is much greater than that due to a positive one. This is, I think, due to the fact that the radiation produced by the positive rays is less penetrating than some of that produced by the cathode ones, so that a much larger proportion of the positive radiation than of the negative is stopped by the celluloid window.

Just as with cathode rays there is a great increase in deflexion when the target is brought forward, so that radiation from it can reach the disk connected with the electrometer; thus the impact of positively electrified particles with metal gives rise to radiation. I showed this by a photographic method many years ago.

The deflexion of the electrometer produced when the target is moved so as to be in sight of the disk connected with the electrometer is in general a larger multiple of the deflexion without the target when the celluloid film is used than with the electrostatic screen. This is, I think, due to the fact that in the latter case the opening through which the rays can pass is a very narrow one while the celluloid window has a much larger area; thus a large proportion of the rays produced by impact with the target will get through the window without any very accurate adjustment of the position of the target, while with the narrow opening only a comparatively small fraction of the rays will get through unless the target is in just the right position.

On the Nature of the Radiation produced by Cathode and Positive Rays.

I have used two methods to investigate the nature of the radiation: the first was to measure the absorption of the metal by thin gold, or aluminium, foil, and the second was to measure the velocity of the electrons ejected from the disk connected with the electrometer when the radiation fell upon it.

Absorption of radiation by thin metallic films.

Films of thin gold and aluminium were interposed in the path of the radiation in the way described in Phil. Mag. xlix. p. 764 (1925), and the consequent diminution in the rate of charging up of the electrometer was measured. Experiments were made on the influence on absorption of the nature of the gases in which the radiation was produced, and of the difference of potential between the anode and cathode of the discharge-tube. The radiations were produced by a stream of cathode rays passing through the gas; as the celluloid window was used, the most absorbable rays were absent. The discharge was produced by a high-potential dynamo made by Evershed and Vignolles, which gave steady potential differences up to 5500 volts.

The thickness of the gold leaf was $7{\cdot}2 \times 10^{-6}$ cm., of the aluminium leaf $5{\cdot}3 \times 10^{-5}$.

Absorption of rays by Gold leaf.

Voltage between cathode and anode.	Ratio of intensity of incident to emergent radiation when the cathode rays passed through.		
	Hydrogen.	Oxygen.	Argon.
1500	...	5·0	
2000	3·8	3·5	
2500	...	3·2	
3000	2·6	2·6	2·6
3500	...	2	2·1
4000	2	2	2·0
4500	1·7	2	
5000	2·8 4·0	1·7	1·5
5500	10	1·6	

In hydrogen the current is very unsteady at voltages higher than 4500, and the appearance of the discharge keeps changing abruptly.

Absorption of rays by Aluminium foil.

Voltage between cathode and anode.	Ratio of intensity of incident to emergent radiation when the cathode rays passed through.		
	Hydrogen.	Oxygen.	Argon.
1500	...	2·1	
2000	2·0	1·8	
2500	...	2·0	
3000	1·9	1·6	1·6
3500	...	1·4	
4000	1·4	1·3	1·7
4500	1·3	1·3	
5000	1·9 2·2	1·4	1·5
5500	8	1·3	

The absorbability of the radiation varies, however, with the kind of electric discharge used to produce it. When an induction coil is used instead of a continuous-current dynamo, the radiation becomes less penetrating even though the length of the equivalent spark-gap may show that the maximum difference of potential produced by the coil is greater than that produced by the dynamo.

We see from the above table that the penetrating power of the radiation generated by the cathode rays increases with the velocity of the rays, though not nearly so quickly as it would if the frequency of the radiation were proportional to the energy of the rays. It does not seem to vary much with the nature of the gas; we shall see, however, that the more absorbable radiations, especially those due to positive rays which cannot penetrate the celluloid film, do vary from one gas to another. The penetrating power of the radiation from the gas was found to be much the same as that of the radiation produced when the same rays were allowed to fall upon a target.

The absorption method of measuring the qualities of the radiation is not applicable to the very easily absorbed radiation which cannot penetrate the thinnest metal foil available, and it is this radiation which is the most important of all in connexion with the theory of electric discharge. I have endeavoured to determine the frequency of this radiation by measuring the velocity of the electrons ejected from a metal plate by the photoelectric action of the radiation. To interpret these experiments it is necessary to consider the theory of the ejection of electrons owing to the photoelectric effects of monochromatic light.

Distribution of energy among the electrons emitted from a plate by photoelectric action.

Let homogeneous radiation fall perpendicularly on a plate of metal, let the mean free path in the metal of the quantum of radiation be λ, then the chance that a quantum is absorbed at a distance between x and $x+\delta x$ from the surface of the metal is proportional to

$$e^{-\frac{x}{\lambda}}\frac{\delta x}{\lambda}.$$

If all directions of projection of the electron by the quantum are equally probable, the chance that the electron is projected in a direction making an angle between θ and $\theta+\delta\theta$ with the normal to the plate is

$$\tfrac{1}{2}\sin\theta\,.\,\delta\theta\,;$$

hence the chance that an electron should start from between x and $x+\delta x$ in a direction between θ and $\theta+\delta\theta$ is proportional to

$$\epsilon^{-\frac{x}{\lambda}}\frac{\delta x}{2\lambda}\sin\theta\,.\,\delta\theta.$$

If E is the energy of the electron at the beginning of its path through the metal, and E_1 the energy after it has travelled a distance l, we know that

$$E^2-E_1^2=\beta l,$$

where β is a constant depending upon the metal. If the electron starts from the depth x in a direction θ, the length of its path in the metal will be $x\sec\theta$ and its energy at the end

$$\sqrt{E^2-\beta x\sec\theta}\,.\quad .\quad .\quad .\quad .\quad .\quad .\quad .\qquad (1)$$

The experimental method is to find whether the electron can escape from the metal and reach an electrode parallel to the metal plate against an opposing difference of potential V_0.

If it is to do this, the energy due to the velocity of the electron at right angles to the plate must be not less than V_0e; hence if E is expressed in the form Ve, we must from (1) have

$$\{V^2e^2-\beta x\sec\theta\}^{\frac{1}{2}}\cos^2\theta\not<V_0e\quad .\quad .\quad .\quad .\qquad (2)$$

Putting $V_0=rV$ and $d=V^2e^2/\beta$, this becomes

$$d-x\sec\theta\not<dr^2\sec^4\theta.$$

Hence the chance of an electron being liberated by the light and escaping from the metal is proportional to

$$\frac{1}{2\lambda}\iint\epsilon^{-\frac{x}{\lambda}}\sin\theta\,.\,dx\,.\,d\theta,$$

where the limits of x and θ are found from the equation

$$d-x\sec\theta=dr^2\sec^4\theta.\quad .\quad .\quad .\quad .\quad .\quad .\qquad (3)$$

Integrating with respect to x we get the term

$$-\tfrac{1}{2}\left[\epsilon^{-\frac{x}{\lambda}}\right]^{d(1-r^2\sec^4\theta)\cos\theta}$$
$$=\tfrac{1}{2}\left(1-\epsilon^{-\frac{d}{\lambda}(1-r^2\sec^4\theta)\cos\theta}\right).$$

Now d is the greatest distance the electron can travel in the metal, and if, as is usually the case, the penetrating power of the radiation is great compared with that of the electrons, d/λ will be small and the preceding expression is approximately equal to

$$\frac{d}{2\lambda}(1-r^2\sec^4\theta)\cos\theta.$$

We have now to find the value of

$$\int \frac{d}{2\lambda}(1-r^2\sec^4\theta)\cos\theta\sin\theta\,d\theta.$$

From equation (3) the limits of θ are 0 and $\cos^2\theta=r$. Using these limits, we find that the value of the integral is

$$\frac{d}{4\lambda}(1-r)^2.$$

Hence the rate at which the electrons escape is proportional to

$$\frac{d}{4\lambda}(1-r)^2.$$

If the energy with which the electrons are liberated by the light quanta is E, and if opposing their escape there is an electric field of potential difference W, and if in addition it requires work measured by P volts to liberate an electron from the metal,

$$r=\frac{\mathrm{W}+\mathrm{P}}{\mathrm{E}}.$$

Hence, if R is the rate at which the electrons escape from the plate,

$$\mathrm{R}=\mathrm{C}\frac{d}{4\lambda}\left(1-\frac{\mathrm{W}+\mathrm{P}}{\mathrm{E}}\right)^2, \quad . \quad . \quad . \quad . \quad (4)$$

where C is a quantity proportional to the intensity of the incident radiation.

Thus the graph representing the relation between R and W is a parabola touching the axis $\mathrm{R}=0$ at the point where $\mathrm{W}+\mathrm{P}=\mathrm{E}$, while that representing the relation between $\sqrt{\mathrm{R}}$ and W is a straight line.

If the radiation is not monochromatic, then, if the intensity of the radiation having quanta with energies between E and $\mathrm{E}+\delta\mathrm{E}$ is $f(\mathrm{E})\delta\mathrm{E}$, then R, the rate of escape of electrons from the metal when exposed to this radiation, is given by the equation:

$$R=\int_{W+P}^{\infty} f(E)\frac{d}{4\lambda}\left(1-\frac{W+P}{E}\right)^{2} dE,$$

$$\frac{dR}{dW}=-\int_{W+P}^{\infty}\frac{d}{2\lambda}\,\frac{f(E)}{E}\left(1-\frac{W+P}{E}\right) dE,$$

and

$$\frac{d^{2}R}{dW}=\int_{W+P}^{\infty}\frac{d}{d\lambda}\cdot\frac{f(E)}{E^{2}}\,dE,$$

$$\frac{d^{3}R}{dW^{3}}=-\frac{d}{2\lambda}\,\frac{f(W+P)}{(W+P)^{2}}\quad\ldots\ldots\ldots\quad(4)$$

Now d and λ are functions of E. We see from equation (1) that d is proportional to E^2, and if we suppose that the absorption of the radiation like that of Röntgen rays is proportional to the cube of the wave-length, λ varies as E^3. On these assumptions,

$$\frac{d^{3}R}{dW^{3}} \text{ varies as } -\frac{f(W+P)}{(W+P)^{3}}.$$

Thus if we determine by experiment the way R varies with W and draw the graph, we can get from it the distribution of the different types of radiation in the incident light; the place where R vanishes will give the greatest frequency occurring in the radiation. If the curve is a parabola the radiation is homogeneous with this frequency, if it is not a parabola the radiation is not homogeneous; the distribution of the intensities can be determined by the preceding equation.

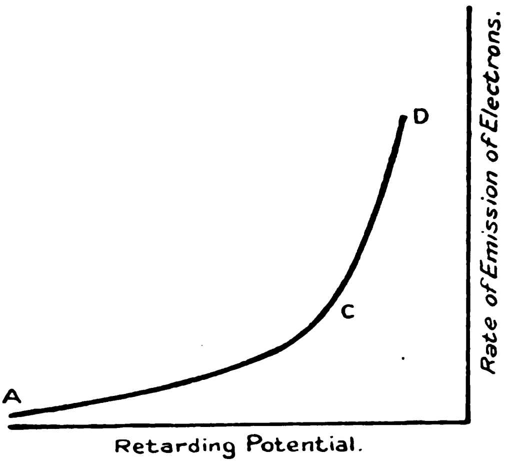
We have assumed that when an electron receives energy from a quantum of light it is as likely to start in any one direction as in any other. The justification for this is the shape of the graphs obtained by experiments.

Along any parabola whose axis is parallel to the axis of y, d^2y/dx^2 is constant and d^3y/dx^3 is zero. Hence we infer from equation (4) that when the graph (fig. 3) for the relation between the rate of emission of the electrons and the retarding potential can through a considerable stretch CD be represented by a single parabola, there is no radiation in the tube whose energy quantum is between the values of W at C and D. This gives a convenient method of determining the character of the radiation from the shape of the graph.

Thus, to take an example, if AD represents the graph, and if AC is one parabola and CD another, we know that the radiation in the tube will be of two types—one having a quantum equal to $W_A + P$, and the other to $W_C + P$, where W_A and W_C are the retarding potentials at A and C respectively, and P is the work required to extract an electron from the metal.

The relation between the rate of emission of electrons and the retarding potential will depend upon the shape of the illuminated electrode and the disposition of the retarding electric field. In our experiments the illuminated electrode was a flat plate and the retarding electric field was that between two parallel plates. If the retarding electric field had been, as in Prof. Richardson's experiments (Phil. Mag. xxiv. p. 575, 1912), that between a large sphere and a small illuminated electrode placed at its centre, then an electron could escape if its total kinetic energy, and not necessarily that part of it due to motion in a particular direction, exceeded rE, and the relation (2) would be replaced by

Fig. 3.



$$\{E^2 - \beta x \sec\theta\}^{\frac{1}{2}} > rE.$$

Using this relation instead of (2), we find that the rate of emission of electrons is proportional to

$$\frac{d}{\lambda}(1-r^2)$$
$$= \frac{d}{\lambda}\left(1-\left(\frac{W+P}{E}\right)^2\right) \quad (\alpha),$$

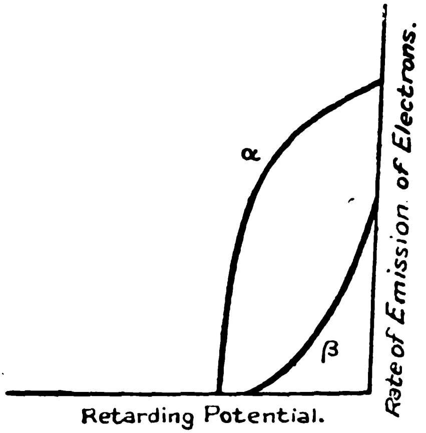
instead of, as in our case,

$$\frac{d}{\lambda}\left(1-\frac{\mathrm{W}+\mathrm{P}}{\mathrm{E}}\right) \qquad (\beta).$$

The graph represented by α is also a parabola, but it is of the type shown in fig. 4 (α), while the graph for β is represented by fig. 4 (β).

With the relation α the slope of the graph vanishes when $r=0$ and is greatest when $r=1$, while with the graph β the slope vanishes when $r=1$ and is greatest when $r=0$.

Fig. 4.



If the radiation were heterogeneous the slope of the α-graph would vanish when $r=0$, though it would not necessarily be greatest at the place on the graph where emission vanished. For the β graph for heterogeneous radiation the slope would vanish when the emission vanished and would be greatest when $r=0$. The graphs in my experiments are always of the β type, and what I think is significant is that though in the majority of cases the graph cannot be represented by a single parabola, there are a few cases, one of which is the radiation given out by the glow next the anode in the discharge through pure oxygen, where the approximation to the parabolic form is very close. This is what we should expect if the radiation were in general heterogeneous, but there are special cases in which it is approximately homogeneous.

Experiments to determine the Distribution of Energy in the electrons emitted by the photoelectric effect of the radiation.

The arrangement used is shown in fig. 2. D is the disk connected with the electrometer by the insulated rod R; this rod is surrounded by a metal tube connected with the earth to shield off electrostatic effects from the disk and its connexions. In front of the disk and parallel to it is a sheet of wire gauze turned back at the ends as in the figure, so as to surround the disk with an equipotential surface When the ends were not turned back I found the results depended to some extent on the distance between the plane of the gauze and that of the disk. I attribute this to some of the electrons escaping through the gap between the gauze and the disk without coming under the influence of the retarding potential. The wire gauze was connected with a battery of storage cells, and differences of potential ranging up to 400 volts could be established between the gauze and the disk; if the gauze were negative with respect to the disk the electric field tended to stop, if it were positive to promote the emission of electrons. The rates of emission of electrons for a series of potential differences were measured by finding the deflexion of the electrometer due to the exposure of the disk to the radiation for a fixed time. The readings with the same difference of potential between the gauze and the disk were fairly constant when the conditions were good, even when the radiation came from a discharge produced by an induction coil. To standardize the readings, the deflexion when there was no potential difference between the gauze and the disk was measured at frequent intervals.

When the coil was working well the deflexions of the electrometer were fairly constant with similar conditions. These investigations, however, brought to light a striking feature of the radiations produced by the discharge: the character of the radiation may change quite abruptly, sometimes without any appreciable change in the appearance of the discharge. I think these changes are due to gases coming off the walls of the tube or to incursions of mercury vapour; later on, experiments are described which show that when heavy gases are introduced into the tube radiations of much higher frequency are added to those already in the tube.

In order that the discharge should be able to pass through the tube the pressure must not be too low; in the great majority of these experiments the pressure was above

01 mm. of Hg, and was thus much higher than that occurring in recent experiments on photoelectric action.

In my experiments a considerable increase in the emission of electrons was produced by putting an accelerating potential on the gauze—*i. e*, the emission was greater when the gauze was positive to the plate than when the gauze and plate were at the same potential.

Another effect frequently observed was that when the gauze was strongly negative to the plate, the plate not merely ceased to lose electrons when exposed to the radiation but slowly acquired a negative charge. The effect was small and soon showed saturation, *i. e.* the rate of increase of the negative charge soon becomes independent of the difference of potential between the gauze and the plate.

This effect might occur if the gas between the gauze and the plate were ionized by the radiation so that a current of negative electricity passed from the gauze to the plate ; it would also occur if some of the radiation were reflected from the disk on to the wires of the gauze so that these gave out electrons by photoelectric action. There are, however, grave difficulties in accepting one or both of these explanations. If the effect were due to the ionization of the gas, then it would increase with the amount of gas surrounding the disk and exposed to the radiation. The apparatus was designed to make this as small as possible, and when the position of the gauze was altered so that the distance between it and the disk was increased and therewith the amount of ionizable gas, the negative effect diminished instead of increasing. Again, if it were due to the reflected radiation it ought to diminish if the surface of the metal in the wire gauze is diminished. I tried the effect of replacing one piece of gauze by another made of much finer wire and more open mesh, but I could not detect any diminution in the negative effect.

The experiments seem to me to indicate that there is at the surface of the disk a layer of ionized gas containing positive as well as negative ions, and that when the gauze is very strongly negative some of the positive ions are pulled out of this layer, so that the disk gets a negative charge. The existence of this retrograde current has to be taken into account in interpreting the graphs, for when the disk neither gains or loses a positive charge it does not necessarily follow that the flow of electrons from it has completely stopped ; it may be that there is still a small flow from the disk which is just balanced by the retrograde current, so that E, the energy given to an electron by the light quantum, will be somewhat greater than the value given by the equation

$$E = W + P,$$

where W is the retarding potential when the disk neither gains nor loses an electric charge.

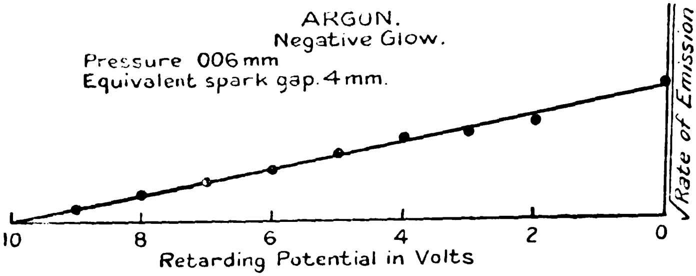
The retarding potential was got from a potentiometer consisting of 100 resistance coils placed in series. The electromotive force on the potentiometer was provided by a battery of small storage cells. To allow for possible variations in the induction coil, readings of the deflexion of the electrometer when there was no retarding potential were taken between those for the different retarding potentials. A convenient way of detecting changes in the character of the radiation is to apply by means of the potentiometer a retarding potential which reduces the flow of electricity to the disk to zero. When the coil is working well, it is possible to get so good a balance that there is not a deflexion of one division on the scale of the electrometer in several minutes. This balance often remained undisturbed when the pressure of the gas in the discharge-tube was altered and with it the potential difference between the electrodes, showing that the limiting radiation did not change appreciably with the physical conditions but was determined by the nature of the gas. If when it is in this state the liquid-air traps which have been used to take out impurities be removed, the balance will suddenly change and it will require a larger retarding potential to stop the flow of the electrons from the illuminated disk, showing that a radiation of a harder type has been introduced, probably arising from the heavier molecules liberated by the removal of the liquid air. This explanation is supported by the fact that the change in the retarding potential required to stop the emission is much more marked than the change in the rate of emission when no retarding potential is applied; this would be the case if a small quantity of radiation of a harder type were produced by some impurity in the gas.

Discussion of the Experiments.

A large number of experiments on the relation between R, the rate of emission from the illuminated copper disk, and W, the retarding potential, were made and the results analysed to find the nature of the radiation. In some cases examples of which are given below, the whole of the graph could be very approximately represented by a single parabola, so that when $\sqrt{R}$ was plotted against W the result was a straight line. Examples of this are given in figs. 5, 6, and 7.

Fig. 5 is for the radiation from the negative glow in argon, the pressure was ·006 mm., the discharge was produced by an induction coil and the equivalent spark-gap was 4 mm. It will be seen that the graph for $\sqrt{R}$ and W is very approximately a straight line and that the emission vanishes when W = 10 volts; thus E, the quantum of energy in the radiation, will be given by

Fig. 5.



$$E = 10 + P + \text{a correction due to the retrograde current.}$$

Taking W as 3·5 volts, this makes the quantum somewhat greater than 13·5 volts.

Fig. 6.

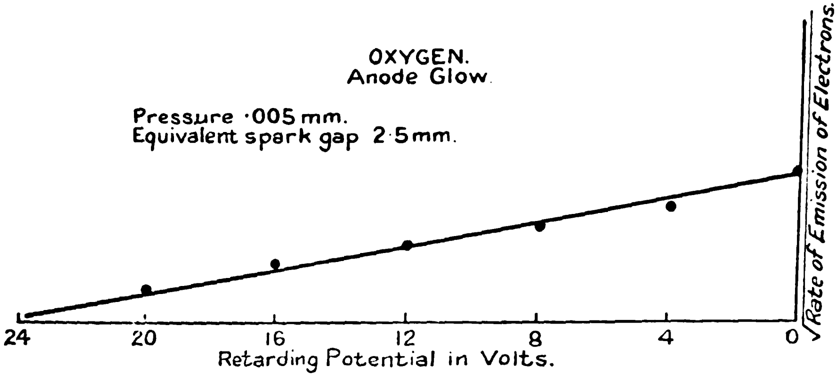


Fig. 6 is the graph for $\sqrt{R}$ and W for the radiation from the anode glow in oxygen at a pressure of ·005 mm.; the discharge was produced by an induction coil and the equivalent spark-gap was 2·5 mm. Again the radiation is approximately homogeneous, and the emission vanishes when the retarding potential is 24 volts.

Fig. 7 is the graph for the negative glow in oxygen when the discharge was produced by a continuous-current dynamo; the potential difference was 400 volts and the current through the tube 2·6 milliamperes, the pressure was ·045 mm.; the emission is stopped by a retarding potential of 12 volts, so that the quantum of radiation is considerably less than in the preceding case.

It is only, however, in exceptional cases that the graph for $\sqrt{\mathrm{R}}$ and W is a straight line throughout the whole of its length; it much more frequently happens that the results for the higher retarding potentials are approximately on a straight line, while those for the smaller ones are far from the prolongation of this line.

Fig. 7.

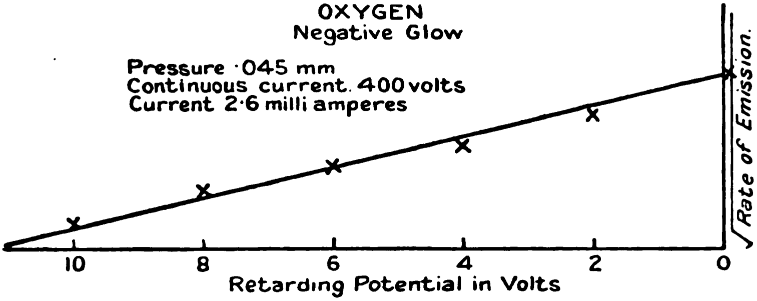


Fig. 8 is the graph representing the relation between R and W for the radiation from the negative glow in the discharge produced by an induction coil through hydrogen at the pressure of ·01 mm. of mercury; the equivalent spark-gap was 4 mm. The unbroken line represents the observations, the dotted lines the two parabolas

$$y = \frac{26\,(10 - \mathrm{W})^2}{100}$$

and $$y = \frac{12\,(2 - \mathrm{W})^2}{4};$$

the sum of the ordinates of these is not distinguishable from the graph on the scale of the diagram. We conclude from this that the radiation was concentrated in two types, one having the energy quantum equal to 10 + P, and the other a radiation of a much softer type with the energy quantum equal to 2 + P.

Fig. 8.

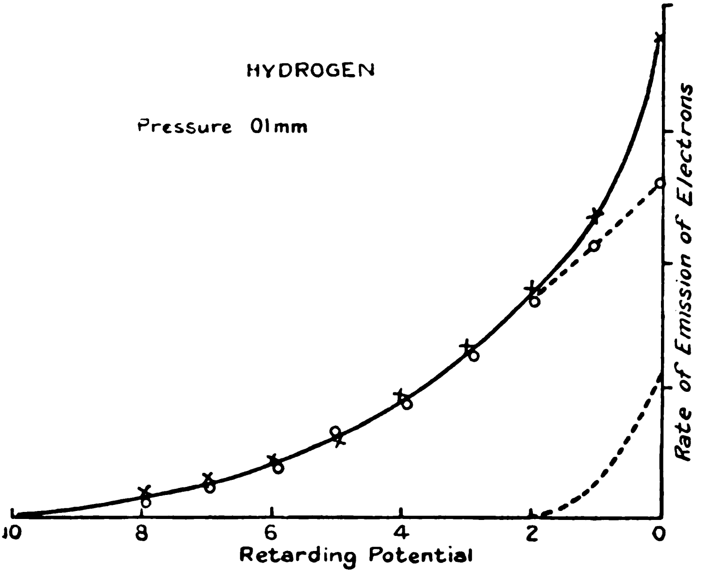


Fig. 9.

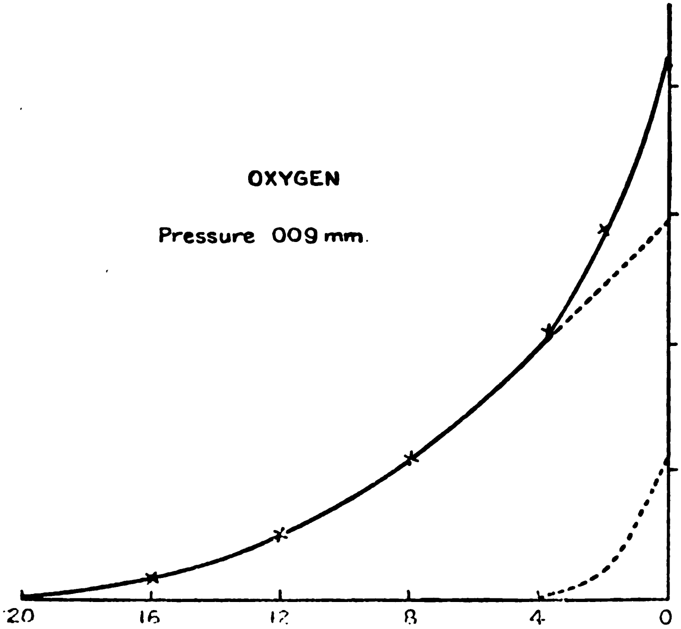


Fig. 9 is the graph representing the radiation from the negative glow in the discharge through oxygen at the pressure ·009 mm. of mercury produced by a large induction coil; the equivalent spark-gap was 4·0 mm.

The graph can be represented by the superposition of the two parabolas

$$R = \frac{39}{256}(20-W)^2,$$

$$R = \frac{25}{16}(4-W)^2.$$

This implies that the radiation consists in the main of two constituents, one having for energy quantum $20+P$ volts, and the other $4+P$ volts.

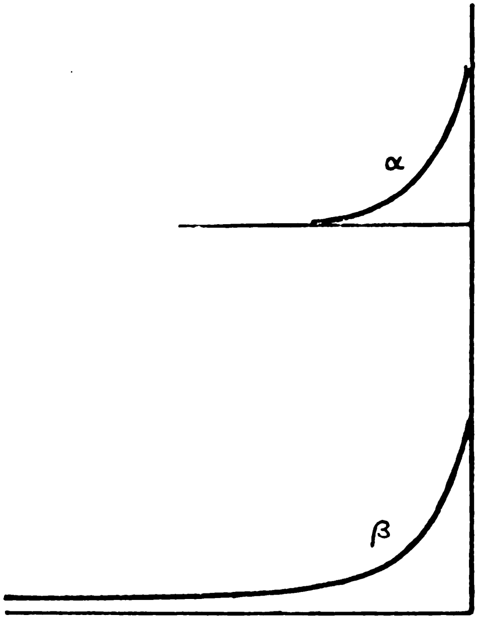
The graphs for the radiation from the negative and anode glows were obtained by using a piece of gauze placed in front of the window through which the radiation passed on its way to the disk connected with the electrometer as the cathode or anode for the electric discharge. With this arrangement the deflexions of the electrometer were very large, and capacities sometimes as large as ·1 microfarad had to be connected to the electrometer to reduce the deflexion to measurable dimensions. The illuminated disk was in this case receiving radiations of the same kind as those which fall on the metal surface of the cathode or anode of the discharge-tube, and as the disk emits copious streams of electrons, it follows that both the anode and cathode in the discharge-tube receive radiation which induces a copious emission of electrons. This emission at the cathode gives rise to the high-speed cathode-rays; while the emission at the anode proceeds until the electrons accumulate in front of the anode in sufficient density to produce a retarding potential sufficient to stop the flow of the electrons. This potential must be equal to that found in the experiments we have just described. The existence of an anode fall of potential was proved many years ago by Skinner, and the magnitude of it was found to be in the neighbourhood of about 20 volts with variations of a few volts depending on the gas in the tube and the nature of the anode. It is thus of the same order of magnitude as the retarding potential necessary to stop the flow of electrons measured in the preceding experiments.

To test whether the effect observed in these experiments was wholly due to radiation coming from the tube and not in part due to uncharged atoms or molecules in an excited state making their way through the screen and then giving out radiation, the disk connected with the electrometer was placed in a side tube so as to be out of the way of radiation from the tube, and by means of a pump a constant stream of gas was drawn from the discharge-tube past the disk: there was, however, no deflexion of the electrometer.

Radiation produced by the passage of Cathode and Positive Rays through Gases.

I have investigated the radiation produced when cathode and positive rays pass through hydrogen, helium, and argon. When the pressure is not lower than ·01 mm. the graphs for the radiation from the cathode and positive rays are not very different; they all showed that the emission of electrons was stopped by retarding potentials which rarely exceeded 12 volts. The analysis of the graphs showed that the radiation was by no means homogeneous. The radiation produced when the positive rays struck against metals gave graphs similar to those due to the radiation produced by the passage of positive rays through the gas. At very low pressures when the potential difference between the anode and cathode is large, there is a distinct difference between the graphs for the radiations from the positive and cathode rays. The graphs for the positive rays are similar to those at the higher pressures and are of the type shown in fig. 10 α, while the

Fig. 10.



graph for the radiation from the cathode rays is of the type of fig. 10 β.

In both cases we have on the application of a small retarding potential a rapid fall in the rate of emission of electrons. With cathode rays, however, this initial rapid fall is succeeded by a stage where the deflexion diminishes only slowly with the retarding potential, and there may be an appreciable emission with a retarding potential as great as 100 volts. With the radiation from the positive rays we have only the stage represented by the rapid fall at the beginning, the emission vanishes when the retarding potential is only a few volts. This indicates that in the radiation from the cathode rays we have a mixture of soft radiation with quanta represented by a few volts with much harder radiation whose quanta may be comparable with a hundred volts. With the positive rays the radiation is all of the softer type.

The production of ionizing radiation by positive rays passing through a gas or striking against a solid has an important bearing on the question of whether or not positive particles ionize by collision. Ionization by positive particles has been observed and measured by Pavlow (Proc. Roy. Soc. A, xc. p. 898, 1914) and others, and has been interpreted as a proof that such particles as well as electrons produce ions by collision. There are, as I have pointed out, very serious theoretical objections to this view, and such results as have been obtained may be explained as due to the radiation emitted by the particles. This radiation will give rise to the emission of electrons from the molecules of the gas and from the surfaces of solids in the discharge-tube, and it is to this and not to direct collisions that we ascribe the ionization observed by Pavlow.

There is still very much that is obscure about the ionization due to positive rays. Seeliger (*Physik. Zeit.* xii. p. 839, 1912) has made quantitative experiments on the subject, and these indicate that the total number of ions produced by a positive ray is but small, very far below the number which would exhaust the kinetic energy of the ray; he found that the number does not vary much either with the speed of the ray or with the pressure of the gas. These results would follow if the ionization were due not to the energy of translation of the particle but to energy internal to the particle, such as might be represented by supposing the particle to contain a limited number of undischarged quanta of radiation, and that it is these, and not the translational energy of the particle, which produce the ionization.

The Electrodeless Ring Discharge.

A copious and convenient source of radiation of the type we are studying is supplied by the electrodeless ring discharge.

When a solenoid is placed in the circuit connecting the outer coatings of two Leyden jars, whose inside coatings are connected with the terminals A, B of an induction coil, when sparks pass between these terminals electrical oscillations are excited and the solenoid is traversed by rapidly alternating currents. If a glass vessel containing gas at a low pressure is placed inside the solenoid, the rapidly alternating currents in the solenoid will by electromagnetic induction produce in the vessel closed lines of electromotive force, and these when the pressure of the gas inside is low produce a ring discharge which is often exceedingly bright. The study of the radiation given out by this discharge has led to some interesting results.

The arrangement adopted was as follows: the solenoid was placed over the tube C in fig. 1 so that the ring discharge is well in sight of the disk used to test the photoelectric effect due to the radiation. Measurements were made on the rate of emission under different retarding potentials. The results seemed to depend to a great extent upon the purity of the gas. With very pure helium or hydrogen a retarding potential of about 12 volts was sufficient to stop the emission of electrons from the illuminated disk, while for oxygen a potential difference of about 24 volts was required. The magnitude of the limiting potential did not seem to vary with the pressure of the gas or the frequency of the discharge. The analysis of the graphs showed that the radiation was not homogeneous. Not infrequently, however, abrupt changes took place in the retarding potential required to stop the emission of electrons, and instead of 12 volts being sufficient, in some cases more than 100 volts were required.

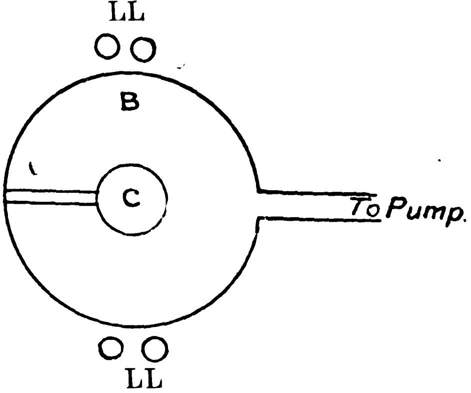
These changes sometimes occurred spontaneously; they could generally be brought about by removing the liquid-air trap used to free the gas from mercury vapour. Though the change in the limiting potentials may be great, there is not a correspondingly large change in the rate of emission of the electrons when there is no retarding potential. It would seem as if the effect were due to the presence of an impurity which emits a much harder type of radiation than that coming from the pure gas.

Radiation from dark electric discharge.

The luminous rings characteristic of the electrodeless discharge appear only when the pressure of the gas is within somewhat narrow limits; but even at pressures lower than those where the luminous radiation appears the electrometer gives large deflexions showing the existence of radiation of smaller wave-lengths than those of visible light. The analysis of this radiation by the method of the retarding potential shows that it is mainly in the region of the radiation which has a quantum of the order of the ionizing potential of the gas.

The following experiment supplies direct evidence of the existence of currents through the gas even when there is no luminosity.

Fig. 11.



C is a bulb containing gas at a pressure at which the luminous discharge is very bright, it is placed inside another bulb B connected with a pump. The coils L L for producing the electrodeless discharge are placed outside B. When the gas in B is at atmospheric pressure there is a bright ring discharge in C; but when the pressure is reduced so that the ring discharge appears in B, that in C disappears. The gas in B is a conductor of electricity and the currents induced in it shield off from C the effects due to the currents through the coils L L. When the pressure in B is reduced so that the vacuum in B is a very high one, the bright ring discharge appears again in C: the induced currents through B are not now sufficient to shield off the effects of the primary current. There is, however, a considerable range of pressure in which, though there is no visible discharge in B, that in C is stopped; showing that there are sufficient currents passing through B without exciting visible luminosity, to shield off the effects of the primary currents. As there would be but little shielding unless the currents passing through the gas were comparable with those which pass through the coil, this experiment shows that large currents may pass through the gas under certain conditions without exciting visible luminosity, though, as we have seen, they do excite radiation of smaller wave-length.

The following calculation shows that when the effect of the primary coil is shielded by the currents in the rarefied gas, a large number of electrons must be present in the gas.

Let us suppose that the coil is a long straight solenoid; consider the free motion of an electron in an exhausted tube coaxial with the solenoid. Let r, θ, z be the cylindrical coordinates of an electron, z being measured parallel to the axis. Then, if H is the magnetic force due to the currents in the solenoid and gas, the electric force at a point distance r from the axis is $\frac{r}{2}\frac{d\mathrm{H}}{dt}$ and is tangential. Hence the equations of motion of a free electron are

$$m\frac{1}{r}\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right)=\left\{\frac{1}{2}r\frac{d\mathrm{H}}{dt}+\mathrm{H}\frac{dr}{dt}\right\}e, \quad . \quad . \quad (1)$$

$$m\left(\frac{d^2r}{dt^2}-r\left(\frac{d\theta}{dt}\right)^2\right)=-\mathrm{H}er\frac{d\theta}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where m is the mass, and e the charge on an electron.

The first of these may be written in the form

$$\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right)=\frac{e}{2m}\frac{d}{dt}(\mathrm{H}r^2),$$

$$r^2\frac{d\theta}{dt}=\frac{e}{2m}.\mathrm{H}r^2+\mathrm{C};$$

if $d\theta/dt$ and H both vanish when $t=0$,

$$r^2\frac{d\theta}{dt}=\frac{e}{2m}\mathrm{H}r^2$$

or

$$\frac{d\theta}{dt}=\frac{e}{2m}.\mathrm{H}.$$

The velocity of the electron at right angles to r is thus

$$\frac{e}{2m}r\mathrm{H};$$

and if ρ is the density of the electrons, the current per unit length of the gas

$$\frac{e^2}{2m}\int_0^a \mathrm{H}\rho r\,dr,$$

where a is the radius of the tube. If N is the number of electrons contained between two planes at right angles to the axis of the tube and unit distance apart,

$$\int_0^a \rho\,.\,r\,.\,dr = \frac{\mathrm{N}}{2\pi};$$

thus the currents through the gas are less than

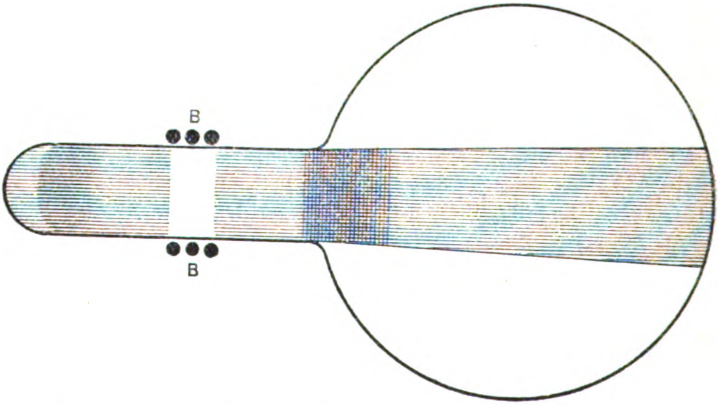
$$\frac{e^2\mathrm{N}\mathrm{H}_0}{4\pi m}.$$

where H_0 is the value of H when $r=a$, if c is the current through unit length of the solenoid,

$$\mathrm{H}_0 = 4\pi c\,;$$

hence the current through the gas is less than $\mathrm{N}e^2/m$ times the current through the coil. If the current through the gas is to neutralize the effect of that through the coils, the magnitude of the gaseous current must not be less than that through the coils, hence $\mathrm{N}e^2/m$ must not be less than unity, since e^2/m is $2{\cdot}8\times10^{-13}$, N must not be less than $3{\cdot}6\times10^{12}$.

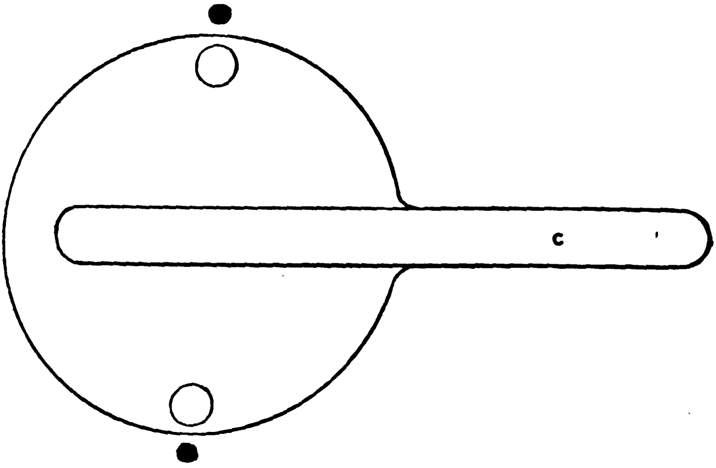
Fig. 12.



The radiation produced by the electrodeless ring discharge is so intense that it is easy to demonstrate its existence by experiments which are suitable for the lecture-room.

One of these is the following. The vessel containing the gas is shaped as in fig. 12. It is a large spherical bulb with a neck about 4 cm. in diameter at one end. The coil for producing the electrodeless discharge is placed round the neck at B, and the bright ring discharge occurs here. Adjoining the ring there is bright luminosity : if the gas is hydrogen, this is a light pink in the layers adjacent to the ring and shows both the Balmer and the second spectrum of hydrogen; this is succeeded by a brilliant red layer showing only the Balmer lines, the boundaries of this layer are fairly well defined. In oxygen the luminosity in the region adjacent to the ring is a brilliant blue. This very bright luminosity only extends a few centimetres from the ring; it is succeeded by fainter luminosity not of the same colour, which can be traced as a luminous cone extending right through the bulb. The glass of the bulb phosphoresces over the area covered by the cone ; this phosphorescence is not of the same colour as that due to cathode rays : another proof that it is not produced by these rays is that the distribution of the phosphorescence is not affected when a magnet is brought near it. The existence of this phosphorescence can be shown by the experiment, fig. 13, where C is a glass tube covered with willemite placed along a diameter of the large bulb in which the ring discharge is produced in a plane at right angles to the tube; when the ring discharge passes

Fig. 13.

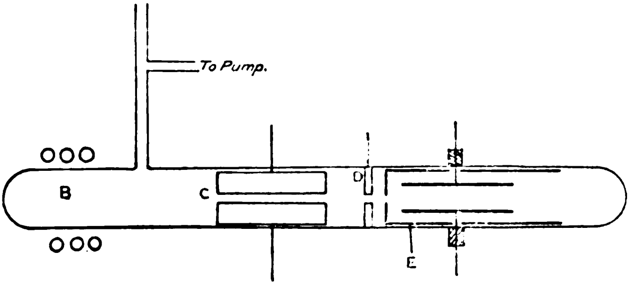


the tube phosphoresces and the distribution of the phosphorescence is not affected by a magnet.

The ionization produced by the radiation can be shown by the experiment represented in fig. 14.

The ring discharge is produced at B. C is the electrostatic filter, consisting of two halves of a brass cylindrical rod, insulated from each other and connected to the terminals of a battery of a large number of small storage cells. D is a brass plug fitting closely into the glass tube, a slit is cut at the centre of this plug so as to be parallel to the space between the two halves of the electrostatic filter. This plug is kept permanently connected with the earth, its object is to shield off any effects due to the high potential of the filter; beyond the plug are two parallel brass plates, so far apart that no radiation passing through the plug can strike against them; one of these plates is connected with the earth, the other to the gold leaves of an electroscope. When the ring discharge is passing at B, the electroscope leaks whether the charge in it is positive or negative, showing that the gas between the plates has been made conductive by the radiation.

Fig. 14.



SUMMARY.

The paper contains an account of experiments on the character of the radiation produced when electric currents pass through gas at a low pressure. The method adopted was to let the radiation fall on a disk of metal and measure the variation in the rate of emission of electrons due to the photoelectric effect when the emission was retarded by an electric field tending to stop the escape of electrons. The theory of the variation of the rate of emission with the strength of the field is worked out, and methods are given for determining from the graph representing the relation

between rate of emission and the potential difference in the retarding field the spectrum of the radiation.

The radiation produced by the passage of cathode and positive rays through the gas, that from the negative and anode glows in hydrogen, oxygen, helium, and argon at different pressures are discussed. It is found that the frequencies of by far the greater part of the radiation are comparable with those corresponding to quanta of the order of the ionizing and resonance potentials of the gas, in the case of the radiation due to the cathode rays these radiations are mixed with others of a higher frequency.

In a few cases the radiation was found to be fairly homogeneous, but in general it is a mixture of radiation having a frequency comparable with that of the ionizing radiation with other radiation of a lower frequency.

The electrodeless ring discharge is found to be a very copious and convenient source of radiation of this type, and various lecture-room experiments are described for demonstrating the existence and properties of the radiation.

I have much pleasure in thanking Mr. E. Everett and Mr. Morley for their assistance in making these experiments.

LX. *Electric Double Refraction in Colloids.*

By YNGVE BJÖRNSTÅHL *.

(From the Laboratory of Physical Chemistry, Upsala.)

[Plate XIII.]

BY accidental double refraction is meant the phenomenon that a medium, during the action of external agents, assumes optical properties similar to those of a uniaxial crystal. Thus the behaviour is not characteristic for the substance *per se* in its non-excited state, but is produced, for example, by a magnetic or an electric field.

The magnetic double refraction in liquids was first studied by A. Cotton and H. Mouton †. In a previous communication the author has given an account of the magnetic double refraction in certain colloids ‡. Analogous to the phenomenon in a magnetic field a double refraction also appears in an electric field. This action has been subjected to detailed investigations and is often called the electric Kerr effect,

* Communicated by the Author.

† *C. R.* cxlv. p. 229 (1907).

‡ Phil. Mag. xlii. p. 352 (1921).

after its discoverer, J. Kerr [*]. Plane polarized light is passed through a medium in a direction perpendicular to the lines of force. The azimuth of the plane of polarization should then form an angle of 45° with the lines of force. The emergent beam is elliptically polarized. The vibrations parallel to and at right angles to the lines of force display a difference in phase and eventually a change of the amplitudes, the two vibrations being absorbed to a different extent. There are two circumstances that characterize the electric double refraction in ordinary liquids: (1) the retardation is proportional to the square of the intensity of the field, and (2) no dichroism is found. The exception recorded by Meslin [†], viz. dichroism in a solution of potassium dichromate in carbon disulphide, may be disregarded since the solution represents a coarse suspension. The time of disappearance of the double refraction in ordinary liquids, *i. e.* the time of relaxation, is very short; according to Abraham and Lemoine [‡] less than 10^{-8} sec.

With reference to colloidal solutions, it is to be noted that de Metz [§] in his investigations of the Kerr effect in conducting liquids made certain experiments with a three-per-cent. gelatine-water solution. This system at ordinary room temperature is a gel, and consequently the nature of the double refraction is dubious. It is not until 1915 that we can record any experiments in the true sense. That the study of the electric double refraction was not begun until so late a period is probably due to the fact that the colloidal systems as a whole were investigated at a comparatively late date; this especially concerns the colloids in dispersion media other than water. Dieselhorst, H. Freundlich, and W. Leonardt [||], while studying vanadium pentoxide sols, found that the sol showed double refraction in an electric field, or in the words of the authors: "auch unter dem Einfluss des elektrischen Stromes tritt unter geeigneten Bedingungen Aufhellung zwischen gekreuzten Nicols auf" [¶]. The present writer, however, was the first to make any measurements on such sols. The experiments were continued later in collaboration with C. Bergholm [**]. Some measurements on gold sols were also made.

---

[*] Phil. Mag. [4] l. p. 337 (1875).

[†] *C. R.* cxxxvi. p. 888 (1903).

[‡] *C. R.* cxxix. p. 206 (1899).

[§] *Journ. de la Soc. Phys.-Chem. Russe*, xxxiv. p. 505 (1902).

[||] 'Elster-Geitel-Festschrift,' p. 476. Vieweg & Sohn, Braunschweig, 1915.

[¶] *L. c.* p. 463.

[**] *Phys. Z.* xxi. p. 137 (1920).

Although this paper is devoted to colloidal solutions in the narrow meaning of the expression, the experiments with coarse suspensions made by Meslin [*] should be cited in this short historical survey. He observed "dichroism" in a suspension of helianthine crystals in carbon disulphide. The experiments were continued by Chaudier [†], who studied the dichroism with the aid of a Soleil polariscope, and the double refraction with a Bravais double-plate. He investigated, for example, such systems as powdered mica suspended in benzene, and gypsum in benzene [‡]. The experimental methods in themselves show only the sign of the double refraction and the direction of the maximum absorption. The investigations of St. Procopiu [§] on suspensions of various mineral powders, such as calc-spar and zircon, follow the same line. The double refraction was measured with a half-shade analyser, not described in his paper. A positive double refraction is ascribed to the difference between the ordinary and the extraordinary refractive index of the crystals; a negative one to the hypothesis that the particles arrange themselves as strings in the field.

Measurements.

A large number of colloids are included in the present investigations. Among these may be mentioned the metal sols of gold, silver, copper, platinum, mercury, molybdenum, tungsten, bismuth, antimony, iron, nickel, and titanium. In addition, however, experiments have been made with sols of non-metallic disperse phase, such as carbon, sulphur, antimony trisulphide, arsenic trisulphide, vanadium pentoxide, starch and gelatine, and many dyestuffs. As a general rule it may be stated that the first of the two above-mentioned groups is characterized by an electric double refraction of negative sign. As to the non-metallic colloids, on the other hand, a rule cannot be given. It cannot be said, however, that the electric double refraction is a property characteristic of all sols. It is possible to trace an effect only at a certain degree of dispersity.

With regard to protected colloids, it may be mentioned in passing that they show less double refraction than do unprotected ones. This applies to Au, Pt, Bi, Fe, Mo, W, Ag, Cu, Ni, C, Sb, Ti, Sb_2S_3, As_2S_3, Fe_2O_3. A number of alcosols also have been examined.

---

[*] *C. R.* cxxxvi. p. 930 (1903).

[†] *C. R.* cxxxvii. p. 248 (1903).

[‡] *Ann. de Chimie*, xv. p. 67 (1908).

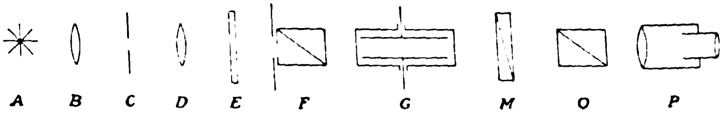
[§] *C. R.* clxxii. p. 1172 (1921). Later on he collected his measurements in the work: 'Sur la biréfringence électrique et magnétique des suspensions,' Thèses, Paris, 1924, in which he also describes some experiments with metal suspensions.

An account is given in the following pages of the electric double refraction in mercury, gold, and sulphur hydrosols.

Apparatus.

Several different experimental arrangements were used, one of which is shown in fig. 1. The lens *B* throws an image of the arc *A* on the rectangular slit *C*, and this image is projected on the objective of the telescope *P* by the lens *D*. The light is passed through the monochromatic filter *E*, a polarizing Thomson-Glan prism *F*, the trough *G*, the compensator *M*, the analysing prism *O*, and, finally, through the telescope *P*. The compensator was of the type designed by D. B. Brace[*] and afterwards employed by many scientists. The arrangement consists of two plates of mica. The first, the compensator proper, covers the whole field of view and is mounted on a graduated circle, the rotation of which can be read. The half shade, or the sensitive strip, consists of a thin sheet of mica inserted in an azimuth of 45° and covering only the centre of the field of vision. This sheet is mounted in balsam between carefully selected cover-glasses free from double refraction. The sensitive strip can be placed either before or after the compensator. The first method is the most frequently used, and has also been used by the author. The principal sections of the polarizing prisms were crossed, and formed an angle of 45° with the lines of force. The telescope was focussed on the sensitive strip, the angle between the principal axis of the latter and that of the prism being 45°. The compensator was turned so as to obtain a uniformly illuminated field of view, the electric field was applied, and the compensator set for a match again.

Fig. 1.



The theory of this compensator has been treated by L. B.

---

[*] Phil. Mag. 6 v. p. 161 (1903.

Tuckerman [*], L. Chaumont [†], and C. Bergholm [‡]. If ψ is the angle between the principal planes of the analyser and of the compensator, and if δ is the angular retardation of the compensator, we obtain

$$\tan\left(\Delta+\frac{\epsilon}{2}\right)=\frac{\sin 2\psi \sin \delta}{1-2\sin^2 2\psi \sin^2\frac{\delta}{2}}, \quad . \quad . \quad . \quad (1)$$

where Δ is the unknown phase difference, and ϵ is the phase difference of the sensitive strip. If $\Delta=0$, we obtain

$$\tan\frac{\epsilon}{2}=\frac{\sin 2\psi_0 \sin \delta}{1-2\sin^2 2\psi_0 \sin^2\frac{\delta}{2}}, \quad . \quad . \quad . \quad . \quad (2)$$

where ψ_0 represents in this case the angle between the compensator and analyser. Subtracting (2) from (1), we have

$$\frac{\tan\Delta}{\left(1-\tan\Delta\tan\frac{\epsilon}{2}\right)\cos\frac{\epsilon}{2}}=$$

$$\frac{2\sin\delta\cos(\psi+\psi_0)\sin(\psi-\psi_0)\left[1-2\sin^2\frac{\delta}{2}\sin 2\psi\sin 2\psi_0\right]}{\left(1-2\sin^2 2\psi\sin^2\frac{\delta}{2}\right)\left(1-2\sin^2 2\psi_0\sin^2\frac{\delta}{2}\right)}.$$

C. Bergholm [§] has shown that the equation (1) is valid independent of the double refraction, being united with the amplitude effect; in other words, if the axis of the ellipse of the emergent light has an azimuth differing from 45°. If suitable approximations are made, we obtain

$$\tan\Delta = 2\sin\delta\cos(\psi+\psi_0)\sin(\psi-\psi_0).$$

Bergholm has also indicated the range over which this approximate formula can be used. If we put $\psi-\psi_0=\theta$, the rotation of the compensator, the expression may be written

$$\tan\Delta = 2\sin\delta\sin\theta\cos(2\psi_0\pm\theta).$$

In order to analyse the elliptically polarized light emerging from the tube G, it is sufficient to measure first the phase difference between the components parallel and perpendicular to the lines of force, then the azimuth of the major axis of the ellipse, the elements of which are defined by this with regard to form and position.

---

[*] *Cf.* University Studies, published by the University of Nebraska, ix. No. 2.

[†] Thèses, Paris, 1914.

[‡] Diss., Upsala, 1915.

[§] *L. c.*

In order to determine the azimuth of the ellipse, a quarter-wave plate was inserted between the tube G and the compensator (*cf.* fig. 1). The plate is rotated to obtain linear polarized light, which is tested with the Brace apparatus. The azimuth of the quarter-wave plate is read. This arrangement is described by Cotton and Mouton [*], who employed it for the study of dichroic circular polarization, by M. G. Bruhat [†], and independently by Bergholm [‡], who has given full particulars about the method. If the liquid is considered to be a uniaxial dichroic crystal, with the axis along the lines of force, then the absorptions of the parallel and of the perpendicular components are different. Calling the rotation of the quarter-wave plate ϕ and the specially determined phase difference Δ, we can derive the ratio ρ of the parallel amplitude to the perpendicular one, $\rho = \frac{a_\parallel}{a_\perp}$ from the equation

$$\frac{1-\rho^2}{2\rho} = \tan 2\phi \cos \Delta.$$

The usual precautions were taken in order to eliminate the error arising from the fact that the quarter-wave plate did not show a phase difference of exactly $\pi/2$. The quarter-wave plate is turned through an angle of 90° and a new reading is taken. The retardation of the plate of mica used as a compensator was determined by the aid of a plate of mica with a retardation amounting to nearly $\lambda/4$. The phase difference of these "$\lambda/4$" plates was determined using a Babinet compensator. The constants of the plate of mica used as compensator are recorded in Table I.

TABLE I.

Constants of the compensator.

λ. (A.U.)	δ.	$2\psi_0$.
7000	7° 2′	
6200	7° 33′	5° 6′
5900	7° 57′	
5460	8° 33′	4° 55′
4360	10° 24′	4° 55′

---

[*] *Journal de Phys.* (5) i. p. 8 (1911).

[†] *C. R.* cliii. p. 248 (1911).

[‡] *L. c.*

In order to define the sign of the double refraction, the medium in the field is regarded as a uniaxial crystal the axis of which is parallel to the lines of force.

The sign of the double refraction is considered as positive when the refractive index n_e for the ray which is polarized in a plane at right angles to the principal section in the crystal imagined (*i. e.* at right angles to the line of force) is greater than the refractive index n_0 for the ray which is polarized in the principal section. Thus, for a positive medium, $n_e > n_0$; for a negative one, $n_0 > n_e$. In the first case the more retarded vibration is propagated in the principal section, whilst in the second it is propagated in the section at right angles.

In some experiments the monochromatic filter was replaced by a monochromatic illuminator.

With regard to the experimental methods, it must be observed that relative measurements, *i. e.* comparison of the double refraction for a colloid and a normal substance, are meaningless on account of the double refraction not being quadratically dependent on the intensity of the field. Otherwise, in the question of the liquids here treated, all of which are conducting to a certain degree, the relative method of Des Coudres * would have been particularly suitable. When using this method it is unnecessary to know the voltage. High-frequency voltage of unknown wave-shape can be used.

For an absolute determination it is necessary to determine the voltage between the plates of the condenser. If such a determination is to have any meaning, the shape of the voltage curve must be known. Direct pressure cannot be used on account of electrolysis. An alternating electromotive force giving a sine-wave must be employed. Further, it is necessary that the frequency be as high as possible. Experiments on the decomposition of very dilute solutions of electrolytes showed an enormous decrease of the electrolysis when the frequency was increased from 200 to 1200 cycles per second. The voltage was obtained from a high-frequency alternator constructed by Hartmann and Braun, Frankfurt am Main. The alternator is supplied with a 48-pole rotor, which is fed by direct current from a storage battery. When the number of revolutions per minute is 3000, alternating current of the frequency of 1200 cycles per second is generated. The alternator is supplied with a distance tachometer of Hartmann and Braun's construction, so that it is possible to read the frequency at the laboratory. The machine is built with special regard to its giving an electromotive force wave of sine shape. The electric double refraction is dependent on the frequency. One of the first tasks was to investigate to what extent the voltage wave supplied by the machine was of sine shape.

---

* *Verh. Ges. Deutsch. Naturforsch. u. Arzte,* 1893 ii. p. 67.

If $f(t)$ is the electromotive force wave of the machine, then by Fourier's theorem we have

$$f(t) = \Sigma a_n \sin n\,\omega t + \Sigma b_n \cos n\,\omega t = \Sigma \sqrt{a_n^2 + b_n^2} \sin (n\,\omega t + \phi_n)$$

$$\tan \phi_n = \frac{b_n}{a_n}.$$

In order to find $f(t)$ we must determine the amplitudes $\sqrt{a_n^2 + b_n^2}$ and their time-lags ϕ_n. In order to measure the amplitudes the method first devised by Pupin[*] was employed. The potential difference, the wave of which is to be analysed, is applied to the terminals of a circuit consisting of a condenser in series with a coreless choke coil. An electrostatic voltmeter is placed across the condenser. The inductance is varied continuously and the voltmeter reading at resonance is noted. In this way it is possible to determine the amplitudes of the various harmonics.

With light load the amplitude of the third harmonic reached a value of 15 per cent. of the amplitude of the first harmonic. The other harmonics were small and could hardly be traced.

In order to eliminate the higher harmonics, a self-inductance and a condenser were connected in series and the potential difference at the terminals of the condenser was used. The arrangement can be considered as a potential divider. At the terminals of the condenser a considerably smaller fraction of the voltage corresponding to the higher harmonics appears than of the voltage corresponding to the first harmonic, answering to the proportion between the effective resistance of the capacity and that of the self-inductance. This proportion varies with the frequency. For the first harmonic the proportion is $1/LC\omega^2$; for the nth one it has the value $1/LCn^2\omega^2$, where L is the coefficient of the self-inductance, C the capacity of the condenser, and ω is 2π times the frequency.

For the proportion between the effective voltage across the condenser of the nth harmonic and that of the first harmonic, we have the expression

---

[*] Journ. of Science, B, xlv. p. 325; B, xlviii. p. 379.

$$\frac{a_n\sqrt{R+\left(L\omega-\frac{1}{C\omega}\right)^2}}{na_1\sqrt{R+\left(Ln\omega-\frac{1}{nC\omega}\right)^2}}.$$

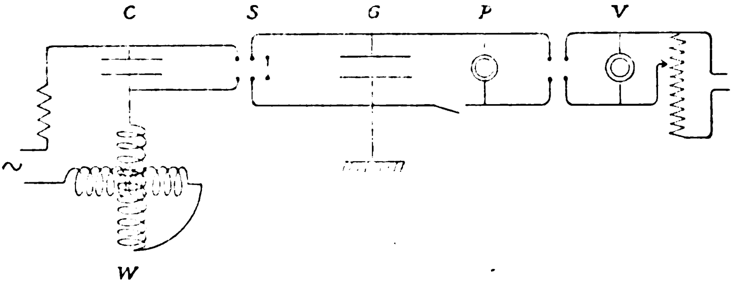
This expression will be a minimum when $\frac{1}{L\omega}=C\omega$.

The voltage was varied by changing the intensity of the current in the rotor, partly by means of an ohmic resistance, which served as a potentiometer.

The capacity consisted of a mica condenser of 1·0 microfarad and the self-inductance of a self-inductometer. The alternator was regulated to give a frequency of 1200 cycles per second, and the inductometer was then adjusted for resonance.

In order to determine the voltage between the plates of the cell, an alternating voltmeter, a dynamometer instrument from Siemens & Halske, was used first. As it was intended for a frequency of about 50 cycles per second, it was graduated with the aid of a quadrant electrometer for the frequency employed, namely 1200 cycles per second. For the measurements the precautions proposed by Orlich * were observed. The quadrant electrometer in turn was compared with a Weston normal cell by means of a potentiometer.

Fig. 2.



Some experiments were made using a Bjerknes-Ebert † electrometer. In most of the measurements a hot-wire voltmeter made by Hartmann & Braun was employed. This was frequently compared with a precision voltmeter manufactured by Siemens & Halske, Berlin. The latter in turn was compared with a Weston normal cell by means of a compensation method.

A diagram of the electrical arrangement is given in fig. 2,

---

* *Z. f. Instr. K.* 1903, p. 97.

† K. Bjerknes, Wied. *Ann.* xlviii. p. 594 (1893).

where *G* is the trough, *C* the condenser, *W* the self-inductance, *S* a switch, *P* the voltmeter, and *V* a checking device for the voltmeter.

The Trough.

Through repeated experiments certain colloids were found to be less stable in metallic vessels. Hence it was necessary to use Jena normal glass as much as possible for the troughs employed in the experiments. This material also facilitates a more satisfactory cleaning of the trough. The condenser plates themselves naturally must be of metal. To reduce to a minimum the metallic surface which comes in contact with the liquid, experiments were made with glass plates plated with silver and then gilded on one side. The attempt failed because common soda glass was used. The idea was discarded at the time, because glass plates of less soluble glass could not conveniently be obtained within a reasonable period. Instead, condenser plates of copper covered with thick gilding were made. The opposite surfaces were ground to a plane.

Fig. 3.

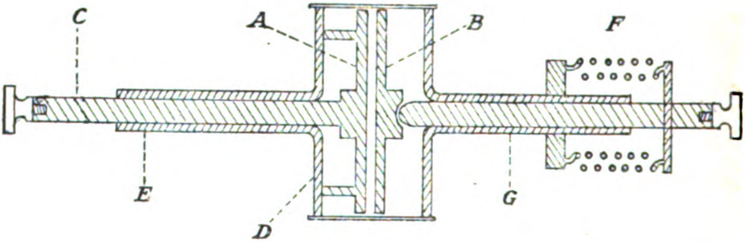


Fig. 3 shows the appearance of one of the troughs in a horizontal section (*cf.* also Pl. XIII.). The plates of metal *A* and *B* are enclosed in the glass tube *D*. The plate *A* is fixed to the cylindrical rod *C*, which is movable, with some play, in the side tube *E*.

The plates are kept apart by four small plates of glass inserted between them. The plate *B* is pressed against the plate *A* by the rod *G* and the spring attachment *F*. It is evident from Pl. XIII. that the trough is supplied with tubes for filling and emptying, together with a tube for the thermometer. On account of the instability of the sols the filling must be repeated for every reading. A convenient arrangement for this was therefore necessary. The sol is contained in a glass flask and is pressed into the trough by compressed nitrogen.

It was very difficult to obtain electrodes free from electrolytes. The galvanically gilded electrodes in particular seemed to have adsorbed large quantities of electrolytes. Only after repeated washings with distilled water, while the condenser plates were subjected to electrical discharges, was it possible to remove the electrolyte.

The distance between the plates is determined by the thickness of the glass plates inserted. This was measured with a micrometer screw gauge, which in turn was checked against Johansson gauges.

Correction of the Length of the Condenser.

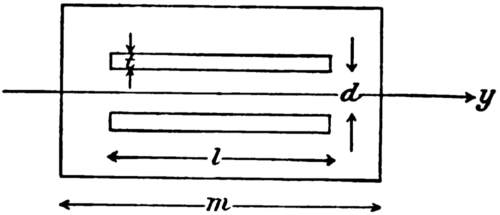
The Kerr constant B is defined by the expression

$$\Delta = 2\pi B l E^2, \quad \ldots \ldots \quad (1)$$

where Δ is the phase difference between the vibration parallel to the lines of force and that at right angles.
l is the length of the condenser (cm.).
E is the intensity of the field (electrostatic units).

At the edge of the condenser plates, however, the field is never homogeneous. Let us suppose that the light passes through an arrangement corresponding to fig. 4, a vessel of length m, and between the condenser plates of length l and thickness t. The distance between the plates is d. The potential difference between the plates is V. The action of the field on a common liquid can be expressed as follows:

Fig. 4.



$$\Delta = 2\pi B \int_{-\frac{m}{2}}^{\frac{m}{2}} E^2 dy. \quad \ldots \ldots \quad (2)$$

This action is equivalent to a homogeneous field of intensity $E_0 = \frac{V}{d}$ and of length l_0:

$$\Delta = 2\pi B l_0 E_0^2. \quad \ldots \ldots \quad (3)$$

Thus l_0 is defined and is evidently independent of the potential difference between the plates.

In the question of the disperse systems treated here, the quadratic law is often not applicable, but a more complicated one instead,

$$\Delta = 2\pi B l f(E).$$

Instead of (2) and (3) we obtain

$$\Delta = 2\pi B \int f(E)\, dy = 2\pi B f(E_0) \times l_0\,;$$

l_0 is a function of E, thus one cannot give any corrected value.

In the case of several colloids, however, the deviation from the quadratic law is slight, and therefore in order to get an idea of the order of magnitude of the correction $l_0 - l$, an estimate was made on the assumption that the expression (1) is valid.

In some preliminary experiments a tube very long in comparison with the condenser plates was used. If $m - l$ (*cf.* fig. 4) is a large quantity, the formula $l_0 - l = \frac{d}{\pi}$ of Lemoine * can be used.

On account of the very strong absorption which frequently occurs, it was necessary to work with as short layers of liquid as possible; so troughs were employed, the end surfaces of which were at a very short distance from the end surfaces of the condenser plates. For this case a correction formula has been given by L. Chaumont †:

$$l_0 - l = \frac{d}{\pi}\left\{1 + \frac{d}{\sqrt{a^2-1}}\log\left(a + \sqrt{a^2-1}\right) - \log\frac{az-1+\sqrt{z^2-1}\,\sqrt{a^2-1}}{z-a}\right\},$$

where z and a are defined by

$$m - l_0 = \frac{d}{\pi}\left\{\frac{\sqrt{z^2-1}}{a^2-1} + \frac{a}{\sqrt{a^2-1}}\log\left(z - \sqrt{z^2-1}\right) - \log\frac{az-1+\sqrt{z^2-1}\,\sqrt{a^2-1}}{z-a}\right\}$$

$$\frac{a}{\sqrt{a^2-1}} = 1 + \frac{2t}{d}.$$

---

* *C. R.* cxxii. p. 836 (1896).

† Thèses, Paris, 1914, p. 161.

For the meaning of the symbols, see fig. 4.

The values of one of the troughs used were as follows :—

$$m = 4{\cdot}04 \text{ cm.}$$
$$l = 3{\cdot}94 \text{ ,,}$$
$$d = 0{\cdot}15 \text{ ,,}$$
$$t = 0{\cdot}10 \text{ ,,}$$
$$l_0 - l = 0{\cdot}33 \text{ ,,}$$
$$l_0 = 3{\cdot}94 + 0{\cdot}03 \text{ cm.}$$

As the correction for the length of the condenser does not reach one per cent., it obviously can be neglected when compared with the other sources of error and with the poorly-defined nature of the medium.

Electric Double Refraction in a Mercury Sol.

A mercury sol was prepared by the method of pulverization according to Bredig*. The experimental arrangement was that described by I. Nordlund†. As dispersion medium, water of conductivity $0{\cdot}8 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ was used. The plane mercury surface served as a negative electrode. The intensity of the current was about 2·8 amperes. The temperature of the water was 1° and at the end of the pulverization 5°. Thus a fairly stable sol was obtained. On p. 66, fig. 11*c*, of Nordlund's paper the distribution curve for a sol prepared according to the same method is reproduced. The sol thus obtained was diluted with water of the same conductivity as that used in the pulverization ; so that the final concentration was $2{\cdot}0 \times 10^{-5}$ gram per cubic centimetre.

The sol shows negative double refraction in an electric field. For the measurements a trough was used with the dimensions :

$$l = 4{\cdot}93 \text{ cm.}$$
$$m = 5{\cdot}04 \text{ ,,}$$
$$d = 0{\cdot}236 \text{ ,,}$$

The wave-length used was K=5750 Å.U. (Filter from Wratten & Wainwright.) The data of the measurements are found in Table II., where P is the potential difference in volts, and Δ is the phase difference in minutes of arc.

---

* *Z.f. Electroch.* iv. p. 514 (1898).

† Inaug.-Diss., Upsala, 1918.

TABLE II.

Electric double refraction in mercury sol.

Wave-length = 5750 Å.U.; Concentration = $2{\cdot}0 \times 10^{-5}$ gram per cubic centimetre.

P. (volts.)	$-\Delta$.	$-\frac{\Delta}{P^2}$.	$-\frac{\Delta}{P}$.
23	70′	0·132	3·0
40	154′	0·096	3·6
50	226′	0·091	4·5
60	261′	0·073	4·3
68	280′	0·061	4·1
100	330′	0·033	3·3
145	396′	0·019	2·7

As will be shown later on, water exhibits a positive double refraction which is a function of the quantity of electrolyte in the solution. The mercury sol showed a conductivity not greater than $2{\cdot}5 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$. As will be shown later (*cf.* Table XII.), a sodium-chloride solution of this conductivity shows a positive double refraction of about 5′ in a field of about 100 volts per 0·236 cm. Nothing is known of the nature of the electrolyte in the sol. It appears probable however, that the double refraction arising from the dispersion medium is slight compared with that in the sol.

Table II. shows that Δ increases with the intensity of the field, but not quadratically, as is the case in common liquids and in gold sols when the intensity is small. It appears more likely that the double refraction is proportional to the intensity of the field.

This very strong double refraction of the mercury sol is especially remarkable. It is generally assumed that these particles are spherical. Thus there should be no question of any effect of orientation. There is the possibility, however, that the particles do not consist of mercury, but of mercurous oxide. I. Nordlund[*] has thoroughly investigated the method of preparation. He found in a sol prepared at a temperature of 110° that the ratio between the quantity of mercurous oxide and the quantity of metal is 1 : 14,000. Hence there is no doubt that the effect should be ascribed to the mercury particles. If double particles occur, one might imagine an orientation on account of the field. It should, however, be remembered that the result of such an orientation should be a phase difference which is quadratically dependent on the intensity. This is not at all the case. A direct electro-optical effect might be possible. It remains, however, to take into consideration the electro-capillary phenomenon first described by Christiansen [*]. A mercury drop surrounded by an electrolyte solution of diluted sulphuric acid becomes deformed if a voltage is applied between two electrodes in the solution. The drop becomes egg-shaped, with the pointed end towards the positive pole. The deformation increases with the intensity of the current.

---

[*] Inaug. Diss., p. 78. Upsala, 1918.

In this connexion the behaviour was observed of a drop of mercury under the influence of alternating voltage. In one experiment a mercury drop surrounded with water of conductivity $0{\cdot}8 \times 10^{-6}$ $\text{ohm}^{-1}\,\text{cm.}^{-1}$ was observed. The electrodes were of platinum and were placed at a distance 1·0 cm. from each other. The diameter of the drop was 0·25 cm. The edge of the drop was examined under the microscope. When alternating current of 1200 cycles per second and a pressure of 150 volts was used, no elongation was noted. (The maximum elongation must be less than 0·0004 cm.) In a solution of sulphuric acid of the concentration 0·223 gram per litre, trembling of the drop was obvious when using a voltage drop of 40 volts per cm., but no elongation could be detected. In a sulphuric acid solution of higher concentration, on the other hand, an appreciable change of shape could be seen. In a solution of the concentration 2·22 grams sulphuric acid per litre, an elongation of 0·020 cm. was observed when the potential difference was 10 volts.

We may conclude from the experiments that it is the intensity of the current and not that of the field which is of importance for the elongation. This agrees with our experience of the change of the surface tension with the intensity of the field.

A possibility exists that it is a question of a directed disturbance of the double layer of the micell, which is covered by a gas-layer on the sides facing the electrodes. The writer certainly has not observed any such phenomenon on mercury drops of microscopic dimensions. Such a disturbance would cause the dielectric constant parallel to the field to be less than that at right angles to the field.

Gold Sols.

When an attempt is made to obtain, by the same means as used with common liquids, an exact value of the phase difference by the aid of repeated measurements on the same portion of colloid, the values obtained gradually decrease. The colloid is changed during the influence of the field. A provisional explanation of this may be the change of temperature caused by the flow of current. The phase difference should decrease with increased temperature. If the liquid in the trough is allowed to cool, it will be found that the original value cannot be reproduced. The colloid must have undergone more fundamental change. Coagulation resulting from a difference in mobility of the micellæ is excluded. Investigations on cataphoresis show that the translational movements of the particles are independent of the size*. These gold sols are characterized by a certain instability when they are brought into contact with molar gold. Perhaps the diminution of concentration at the electrode plates, owing to the precipitation, is the cause of the phenomenon. This diminution is perhaps equalized in the whole volume of the liquid through diffusion and convection currents.

---

[*] *Annal. d. Phys.* [4] xii. p. 1072 (1903).

For the measurements on the gold sols a trough of the following dimensions was used :—

Length of trough m	(*cf.* fig. 4)	$=4{\cdot}04$ cm.
„ „ plates l	„ „	$=3{\cdot}94$ „
Distance between plates d	„ „	$=0{\cdot}165$ „
Thickness of plates t	„ „	$=0{\cdot}10$ „

Preparation of the Gold Colloids.

In order to prepare the gold sols, specially purified water was used. Ordinary distilled water was redistilled, first with the addition of potassium permanganate and sulphuric acid, then with the addition of barium hydroxide, and finally in an apparatus of Jena glass. The conductivity of the water obtained in this way was about 1×10^{-6} ohm^{-1} cm.$^{-1}$. All the sols were prepared in flasks of Jena glass, which, after being carefully cleaned with boiling aqua regia and chromic acid, were finally boiled with distilled water. To obtain the sols, Zsigmondy's nuclear method was employed, using the following solutions :—

$HAuCl_4$	0·01 mol. per litre.
K_2CO_3	0·1 mol. per litre.
H_2O_2	30 per cent. (perhydrol from Merck).

A saturated solution of phosphorus in ether, diluted to 1/5.

---

* *Cf.* The Svedberg and Hugo Anderson : *Koll. Zeitschr.* xxiv. p. 156.

The first colloid in a series was prepared using the phosphorus solution as a reducing agent, the following with the aid of the hydrogen peroxide solution. The latter reaction has been studied by F. Doerinckel * and A. Vestgren †. The sol No. 1 was prepared according to the following scheme:—

$HAuCl_4$ solution ...	1	cubic centimetre.
K_2CO_3 ,, ...	0·5	,, ,,
Water	98·5	,, ,,
P-solution	0·5	,, ,,

After the lapse of about twelve hours the solution was boiled in order to remove the ether, and a current of filtered air was passed through it in order to oxidize the phosphorus. Then a few cubic centimetres of water were added to obtain a sol containing $1·96 \times 10^{-5}$ gram gold per cubic centimetre. The product was a sol of a characteristically light red colour. Starting from this nuclear liquid a series of colloids was produced with increasing size of particle. Thus sol No. 2 was prepared with the aid of No. 1 as a nuclear sol. Generally speaking, if

r_i = the radius of the particles in the nuclear sol (mμ);
r_j = ,, ,, ,, ,, resulting sol (mμ);
y = ,, volume of nuclear sol (cubic centimetres);
x = ,, ,, $HAuCl_4$,, ,,
m = ,, ,, the mixture ,, ,,
C = ,, concentration of $HAuCl_4$ (gram gold per cubic centimetre);
c_j = ,, ,, the nuclear sol ,, ,,
c_i = ,, ,, ,, resulting sol ,, ,,

we obtain x and y by the equations

$$y = m \frac{c_j}{c_i} \left(\frac{r_i}{r_j} \right)^3,$$

$$x = m \frac{c_j}{C} \left(1 - \frac{y}{m} \frac{c_i}{c_j} \right).$$

---

* *Zeitschr. f. anorg. Chemie*, lxiii. p. 344 (1908).
† *Zeitschr. f. anorg. Chemie*, xciii. p. 151 (1915).

Thus the scheme for the preparation of the sol No. j appears as follows :—

y cubic centimetres nuclear solution;
x „ „ $HAuCl_4$;
$(m-y-x)$ „ „ water;
2 drops hydrogen peroxide per 100 cubic centimetres solution.

The sols investigated contained $1{\cdot}96 \times 10^{-4}$ gram gold per cubic centimetre.

TABLE III.

Electric double refraction in gold sol.

Wave-length = 5900 Å.U. ; Concentration = $1{\cdot}96 \times 10^{-5}$ gram gold per cubic centimetre ; Diameter $2r = 106$ mμ.

P. (volts.)	$-\Delta$.	$-\frac{\Delta}{P^2}$.
7·9	9′·4	0·15
11·6	27′·9	0·21
17·1	55′·6	0·19
21·6	86′·1	0·18
30·0	133′	0·15
35·0	171′	0·14
45·0	205′	0·10
51·2	216′	0·083
66·0	233′	0·053
84·0	242′	0·032

In Table III. and fig. 5 some data are shown relating to the effect of the potential difference on the electric double refraction in a coarse-grained sol, $2r = 106$ mμ [*]. In fig. 5 the potential differences P, measured in volts, are plotted as abscissæ, and the phase differences Δ as ordinates. Δ is given in minutes of arc. The double refraction is negative. For small values of the potential difference the phase difference is approximately proportional to the square of the intensity, but afterwards approaches a saturation value. The

---

[*] mμ = millimicron = 10^{-7} cm.

Fig. 5.

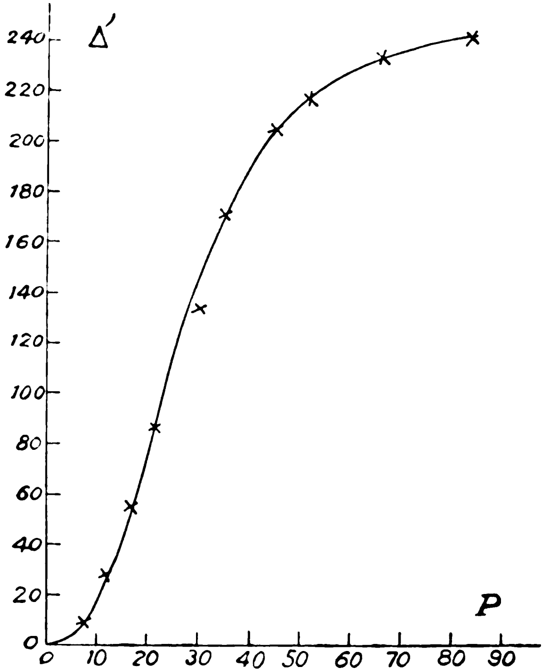


TABLE IV.

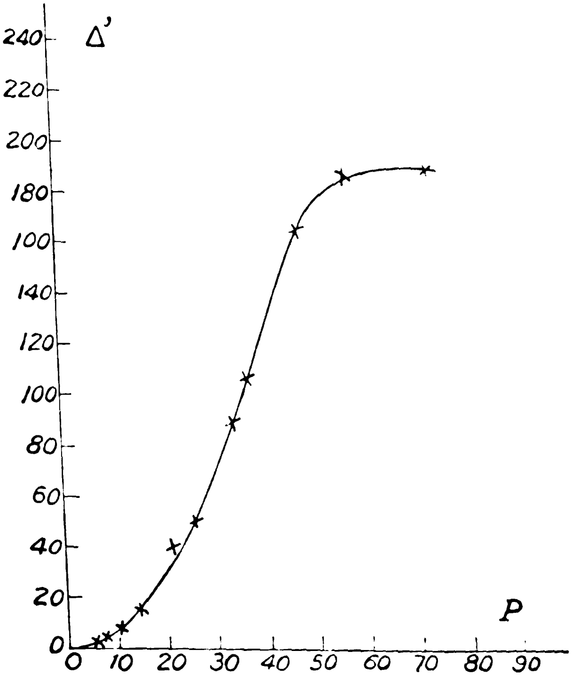
Electric double refraction in gold sol.

Wave-length = 5900 Å.U.; Concentration = $1\cdot96\times10^{-5}$ gram gold per cubic centimetre; Diameter $2r=53$ mμ.

P. (volts.)	$-\Delta$.	$-\frac{\Delta}{P^2}$.
5·2	3′·4	[0·13]
7·8	4′·1	0·067
10·1	9′·7	0·086
14·8	14′·7	0·067
21·6	37′·8	0·081
26·0	50′	0·075
34·0	89′	0·077
38·0	105′	0·073
48·0	164′	0·072
57·5	186′	0·056
74·3	188′	0·054

measurements were carried out with the use of the wave-length 5900 A.U. Table IV. and fig. 6 represent the values which were obtained from observations on a sol of high dispersity, $2r=53$ mμ. Even here saturation sets in.

Fig. 6.



The influence of the size of the particles is very pronounced. Whereas sols with the particle coefficient $2r=5$ mμ and $2r=15$ mμ showed hardly any measurable effect at a potential difference of 20 volts, for a sol characterized by $2r=53$ mμ a value of $\Delta=38'$ was found, and for a sol $2r=106$ mμ a value of $\Delta=86'$. For sols containing particles of the size 200 mμ the double refraction under the same conditions attains a value of $\Delta=5°$. A series of measurements illustrating the variation of the effect with change in size of particle are recorded in Table V.

The change of the double refraction with wave-length is also striking. Only one diagram illustrating the dispersion is reproduced here (Table VI. and fig. 7). The effect shows a very distinct maximum at about 6000 Å.U. The wave-length was varied by means of the monochromatic illuminator.

TABLE V.

Variation of electric double refraction with size of particles.

Wave-length $\lambda = 5900$ Å.U.; Concentration $= 2{\cdot}0 \times 10^{-5}$ gram gold per cubic centimetre; Temperature 17°·5 C.

$2r$. (mμ.)	P. (volts.)	$-\Delta$.	$-\frac{\Delta}{P^2}$.
130	13·6	39′·0	0·39
”	20·2	123′·0	0·30
65	13·4	29′·0	0·16
,	19·2	59′·2	0·16
32	12·6	5′	0·031
,	18·6	6′	0·017
20	18·4	1′	0·003

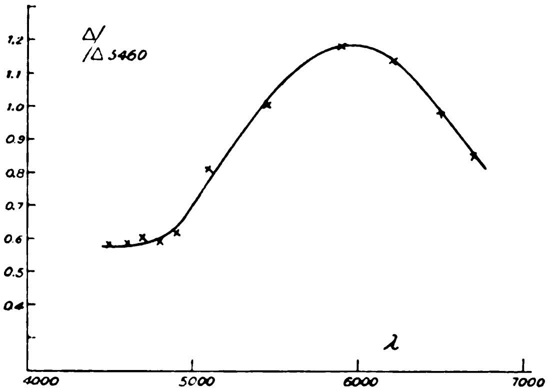
TABLE VI.

Dispersion of double refraction in gold sol.

Potential difference $P = 23{\cdot}9$ volts; Diameter $2r = 106$ mμ; Concentration $= 0{\cdot}98 \times 10^{-5}$ gram per cubic centimetre.

Wave-length. (Å.U.)	$-\Delta$.	$\Delta/\Delta 5460$.
6700	30′	0·85
6500	34′	0·98
6220	40′	1·14
5900	41′	1·18
5460	35′	1·00
5100	28′	0·81
4900	22′	0·61
4800	21′	0·59
4700	21	0·60
4600	20′	0·58
4500	21′	0·59

Fig. 7.



Sulphur Sols.

In the following an account is given of some measurements on a colloid, or more properly, a suspension, with a non-metallic disperse phase, viz. sulphur. The sols were prepared according to Pihlblad's[*] homœopathic method. The same trough that had been used for the gold sols was employed for the measurements. Some data are given in Table VII. The double refraction is negative. The suspension contained $8{\cdot}0 \times 10^{-5}$ gram sulphur per cubic centimetre. The particle coefficient was $2r = 360$ mμ. The wave-length of the light used was 5900 Å.U. Here the deviation from the quadratic law can be traced. Δ/P^2 decreases with the potential difference.

TABLE VII.

Electric double refraction in sulphur sols.

Wave-length = 5900 Å.U.; Concentration = $8{\cdot}0 \times 10^{-5}$ gram sulphur per cubic centimetre; Diameter $2r = 360$ mμ.

P. (volts.)	$-\Delta$.	$-\frac{\Delta}{P^2}$
4·0	0′	0
7·6	16′	0·28
11·6	37′	0·27
13·6	39′	0·21
15·4	46′	0·19
17·1	58′	0·20
19·2	67′	0·18
22·9	71′	0·10
26·6	69′	0·10
16·0	49′	0·19

---

[*] *Cf.* N. Pihlblad, Dissertation, Upsala, 1918.

In Table VIII. some values of the electric dichroism are given. The component parallel to the field is mostly absorbed. Tables IX. and X. represent data from experiments with a more fine-grained sol containing $4\cdot1\times10^{-6}$ gram sulphur per cubic centimetre and of the particle coefficient $2r=190$ mμ. The effect here is considerably less than in the previous solution. It should be observed that a maximum phase difference exists for a certain potential difference. The phenomenon can be attributed to the double refraction of water.

TABLE VIII.

Electric dichroism of sulphur sol.

Wave-length = 5900 Å.U.; Concentration $=8\cdot0\times10^{-5}$ gram sulphur per cubic centimetre; Diameter $2r=360$ mμ.

P. (volts.)	ϕ.
20·0	0
34·0	12′
53·0	48′

TABLE IX.

Electric double refraction in sulphur sol.

Wave-length = 5900 Å.U.; Concentration $=4\cdot1\times10^{-6}$ gram sulphur per cubic centimetre; Diameter $2r=190$ mμ.

P. (volts.)	$-\Delta$.	P. (volts.)	$-\Delta$.
3·6	0′	17·5	4′
5·6	0′	27·0	9′
9·1	0′	37·0	12′
13·0	0′	45·0	13′
18·4	5′	56·0	11′
21·6	8′	102·0	9
27·4	8		

TABLE X.

Electric dichroism of sulphur sol.

P. (volt.)	ϕ.
35·0	4′
76·0	18′

P-*Azoxyphenetol Sol.*

The systems obtained by pouring an alcoholic solution of *p*-azoxyphenetol into water are characterized by the size of the particles, which can be varied by changing the concentration of the alcoholic solution, and further by the length of time the sol is preserved. The nature of these sols is not fully established. Does the disperse phase consist of crystals or is it still liquid? Certain coagulation experiments seem to hint at the possibility of the latter alternative; the particles in the sol would thus consist of liquid—it would be an emulsion. Now *p*-azoxyphenetol belongs to those substances which between certain limits of temperature become crystalline liquids. It would then be a matter of a disperse system with particles consisting of under-cooled crystalline liquid.

In an electric field such sols show a very strong double refraction of negative sign, which is considerably greater than that obtained even with a rather coarse-grained sol obtained by the method of Pihlblad*.

Double Refraction of the Dispersion Medium.

An account has been given in the preceding pages of the electric double refraction in gold, mercury, and sulphur sols. Only these three typical cases are considered here, for the following reasons:—

When discussing the double refraction of a colloid it is necessary first of all to discuss the effect which arises on account of the disperse phase and the dispersion medium separately. The Kerr constant for common liquids is, however, of such an order of magnitude that the Kerr effect in the weak fields here used can be neglected. Direct experiments with conductivity water and with very dilute solutions showed, however, a number of anomalies. The double refraction is strong and a function of the concentration of the electrolyte. Probably we can obtain an idea of the latter in a colloidal solution from the electrical conductivity. Unfortunately the investigations on water were not made until after those on the double refraction of the sols were already completed.

It was found, when investigating the double refraction in certain gold sols, that the sign of the phase difference was negative at first but afterwards became positive. Such a sol contains particles of the size $2r = 106$ mμ. Fig. 8 illustrates the phenomenon when the voltage between the condenser plates was 36·0 volts. The double refraction first increases, then reaches a maximum on the negative side, decreases to zero, and lastly assumes a definite positive value. The reverse is the case when the voltage is switched off and the plates are grounded, this being illustrated by fig. 9. The phase difference first increases, reaches a maximum, and thereafter falls to zero. The process strikes one as being very curious. The form of the curve indicates that there are two concurrent phenomena. A systematic fractional sedimentation showed that there could be no question of two kinds of particles. Hence the phenomenon must be ascribed to the antagonism between the double refraction of the disperse phase and that of the dispersion medium. Now it is known that water shows positive double refraction *, but the results obtained are very dubious on account of the considerable conductivity. According to W. Schmidt † we have for the Kerr constant of water

---

* *L. c.* p. 46.

Fig. 8.

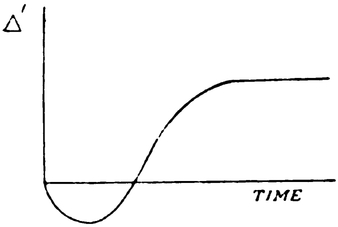
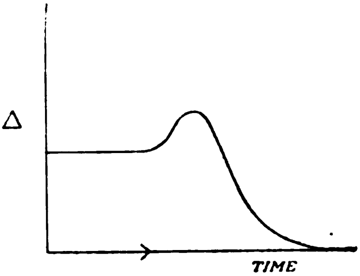


Fig. 9.



$$B = B_0 \times 1{\cdot}0,$$

where B_0 is the constant for carbon disulphide, for which we may assume a value

$$B_0 = 3{\cdot}2 \times 10^{-7} \ddagger.$$

In a field of intensity $E = 100$ volts per 0·25 centimetre we may expect a phase difference of

$$\Delta = 2\pi B l \left(\frac{E}{300}\right)^2,$$

amounting only to about 0′·06 [$l = 5{\cdot}0$ cm.]. It may be said that the most characteristic feature of the Kerr effect is its

---

* *Cf.* J. Kerr, Phil. Mag. (5) xiii. pp. 153 & 248 (1882).
† *Annal. d. Phys.* vii. p. 142 (1902).
Cf. L. Chaumont, Thèses, Paris, 1914.

very short time of appearance. Abraham and Lemoine[*] have shown that for carbon disulphide the time of appearance is less than 10^{-8} second. Later on, James[†] has shown that the disappearance of the double refraction may be supposed to be instantaneous. Thus the conclusion could not be drawn that the form of the curve depended upon the concurrence between a negative double refraction, due to the colloidal particles, and a positive double refraction due to the common Kerr effect in the dispersion medium. Therefore an investigation was begun on the behaviour of water in an electric field, and some very peculiar phenomena were discovered. Common distilled water from the supply of the laboratory, with an electrical conductivity of $4{\cdot}3 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$, showed greater double refraction than water prepared with special care, the conductivity of which was reduced to $0{\cdot}85 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$. In other words, the phase difference is a function of the conductivity of the electrolytic concentration.

Using water of conductivity $0{\cdot}80 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$, a series of sodium-chloride solutions of a concentration varying between 0 and 5×10^{-4} N. was prepared, and the electric double refraction of these was studied. A trough was used with the following dimensions:—

Distance between plates d = 0·236 centimetre.
Length of plates l = 4·94 ,,
Depth of liquid layer L = 5·04 ,,

The wave-length of the light used was 5900 Å.U. The data are reproduced in Tables XI.–XVII. It is evident from Table X. that the double refraction of the pure distilled water does not reach a definite value at once. The increase with time is here, however, comparatively insignificant. At a higher concentration this increase becomes more evident. In a $2{\cdot}0 \times 10^{-4}$ normal sodium-chloride solution, for example, the phase difference is $7'{\cdot}8$ after a lapse of 5·0 seconds, and $27'{\cdot}2$ after 45 seconds. Now, it must be remembered that the solution is heated by the current. Considering the influence of the temperature we have, according to Langevin's[‡] theory, which at least approximately accounts for the conditions involved, $B = \frac{A}{T}$, where B is the Kerr constant and A is a constant independent of temperature T.

---

[*] Cf. *C. R.* cxxix. p. 206 (1899).
[†] *Ann. d. Phys.* iv. p. 954 (1904).
[‡] *Le Radium,* vii. p. 251 (1910).

TABLE XI.

Electric double refraction of water.

Wave-length = 5900 Å.U.; Conductivity = $0{\cdot}85 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$; Potential difference = 100 volts.

Time. (sec.)	Δ.
15	1′·6
30	3′·1
45	2′·9
75	3′·4
90	3′·7
120	3′·7

TABLE XII.

Electric double refraction of $0{\cdot}1 \times 10^{-4}$ *normal sodium-chloride solution.*

Conductivity = $2{\cdot}34 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$; Potential difference = 100 volts.

Time. (sec.)	Δ.
10	5′·7
30	8′·1
45	8′·1
60	7′·8
90	7′·8
120	7′·8

TABLE XIII.

Electric double refraction of $0{\cdot}5 \times 10^{-4}$ *normal sodium-chloride solution.*

Conductivity = $6{\cdot}7 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$; Potential difference = 100 volts.

Time. (sec.)	Δ.
5	4′·7
20	15′·2
30	15′·2
45	13′·8
60	13′·8
120	13′·8

TABLE XIV.

Electric double refraction of 10×10^{-4} *normal sodium-chloride solution.*

Conductivity $= 12{\cdot}3 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$;
Potential difference $=100$ volts.

Time. (sec.)	Δ.
5	7′·3
15	17′·6
30	20′·4
45	23′·0
60	20′·4
90	17′·8
120	20′·1

TABLE XV.

Electric double refraction of $2{\cdot}0 \times 10^{-4}$ *normal sodium-chloride solution.*

Conductivity $= 22{\cdot}1 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$;
Potential difference $=100$ volts.

Time. (sec.)	Δ.
5	7′·8
30	30′·8
45	27′·2
75	27′·2
90	23′·5
120	27′·2

TABLE XVI.

Electric double refraction of 5×10^{-4} *normal sodium-chloride solution.*

Conductivity $= 50{\cdot}6 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$;
Potential difference $=100$ volts.

Time. (sec.)	Δ.
5	17′·5
30	28′·0
90	22′·2
120	28′·2

TABLE XVII.

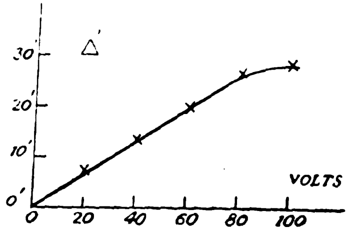
Electric double refraction of 5×10^{-4} *normal sodium-chloride solution.*

Conductivity $=50{\cdot}6\times10^{-6}$ ohm^{-1} cm.$^{-1}$.

Potential difference. (volts.)	Δ.
20·0	7′·6
40·0	13′·3
60·0	19′·8
80·0	26′·6
100·0	28′·0

In the case of the common Kerr effect, a decrease of the double refraction should occur with increased temperature. Thus it must be another phenomenon, and the dependence of the effect on the intensity of the field also shows this. Table XVII. shows (*cf.* also fig. 10) that the phase difference is nearly proportional to the potential difference, while with the common Kerr effect the quadratic law holds true. In Table XVII. the phase difference is recorded as measured 30 seconds after the voltage has been applied.

Fig. 10.

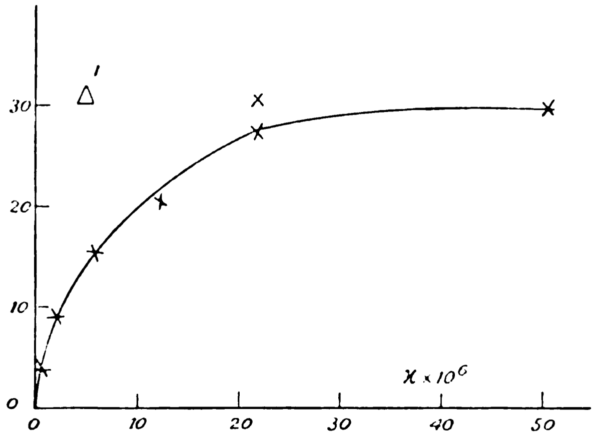


The influence of the conductivity is very surprising. Fig. 11 shows the double refraction, measured 30 seconds after the voltage has been applied. The phase differences are plotted as ordinates and the conductivities as abscissæ. The double refraction rises with the concentration and the conductivity, from the slight value corresponding to the distilled water to a value of saturation answering to the more concentrated solutions.

The determinations made are more of an orientating character, and it is perhaps premature to advance any theory in respect to the phenomenon. It is not probable that the Na or Cl ions could directly give rise to double refraction. The concentration of the ions is very insignificant. The effect probably is connected instead with the hydration of the ions, and the migration of these large aggregates through the liquid. The water molecules along the path of the aggregates are oriented. The author has previously advanced the same hypothesis in regard to certain crystalline liquids *.

On the whole it is a delicate matter to make measurements on liquids of a conductivity of this magnitude. As a matter of fact, colloids in general contain a certain, even if a small, quantity of electrolyte. It is therefore necessary to find out the behaviour of the dispersion medium with addition of electrolytes before attempting to estimate the combined effect.

Fig. 11.



Through consideration of the very peculiar double refraction in water it is easy to explain the strange curves of relaxation in the case of gold sols (*cf.* figs. 8 and 9). The negative double refraction which appears when the voltage is applied can be attributed to the gold particles. Gradually the positive effect from water sets in, and the resulting phase difference becomes zero and eventually positive, all of which depends upon the gold concentration, the degree of dispersity, and the concentration of electrolyte. A reverse process takes place when the voltage is cut off.

There are many different problems which remain to be examined, but mention will be made of only one, viz. the coagulation. Owing to the conductivity being considerable the disturbances are also large. It is necessary to examine the double refraction of the electrolytes before the curves of the colloids can be discussed. Therefore no values will be given here. Perhaps a higher frequency than 1200 cycles per second is necessary to prevent the decomposition.

---

* Cf. *Ann. der Phys.* (4) lvi. p. 202 (1918).

Further mention may be made of some investigations of systems with the same disperse phase but different dispersion media. Here should be obtained a relation with the dielectric constant. Other questions are the variation of the effect with the wave-length, *i. e.* the dispersion and the influence of temperature and time.

In the preceeding tables were given the potential difference P and also the distance between the plates d, but not the intensity of the field E. For these conducting liquids one is not justified, without further investigation, in putting $E = \frac{P}{d}$ for a point in the liquid. A considerable potential drop may occur at the electrodes. Some experiments have been made in order to analyse this problem by varying the distance d between the plates, but no definite results have been obtained on account of the instability of the systems used.

It seems obvious that the electric double refraction may be attributed to an orientation of particles of asymmetrical shape or structure. Let us only consider the first case: isotropic particles of asymmetrical shape. The influence of the forces acting on the particle should then be analysed. In the field the largest axis of the ellipsoid has a tendency to place itself parallel to the lines of force. This is one possibility. Now the particle is charged. Cataphoresis takes place owing to the influence of the field. We know that a body of asymmetrical shape moving in a liquid tends to place its greatest axis at right angles to the direction of the movement. Thus two concurring forces act upon the particle. By comparison with certain experiments on mechanical double refraction [*] it can be decided that a negative double refraction in gold sols points towards an orientation of the greater axis parallel to the lines of force. "Points towards" is written intentionally; many sols, for example mercury or platinum, which show no trace of flowing effect, still exhibit a pronounced negative electric double refraction. An asymmetrical shape of these particles cannot at present be determined by experiment and is rather improbable in mercury sols. It is necessary to conclude that, at least in certain cases, an electro-optical effect in the classical sense is not impossible. The experiments carried out on double refraction of gold sols with the addition of gelatine show the existence of a time of relaxation. Gelatine sols and gels, however, also show electric double refraction, but of the opposite sign, and they exhibit, besides, very disturbing phenomena: a strong formation of striæ. In any case the experiments show that orientation plays an important role, at least in the case of gold sols.

---

[*] *Cf.* Phil. Mag. xlii. p. 362 (1921).

A further support for this is the fact that the dispersion curve shows an evident similarity to that of the magnetic double refraction. The author has shown that the latter phenomenon is caused by an orientation *. From the above point of view it is not difficult to advance a theory on the electric double refraction corresponding to the writer's theory for the effect in a magnetic field †. On account of the complexity of the electric double refraction, however, the theory is not given here.

It is obvious that the phase difference in the question of gold sols (*cf.* fig. 6) approaches saturation with increasing intensity of the electric field. Considering the different factors, we may imagine, for example, that the parallel orientation of the particles begins to reach completion under the influence of the field. Another alternative is that the cataphoretical action plays a part, which tends to orientate the particle at right angles to the field. Finally, the effect in the dispersion medium is very important. The latter is positive for water, and it is here that we must search for the fundamental reasons for the deviation from the quadratic law.

As a final remark, it may be stated that the electric double refraction in colloids is of great interest, but in itself has not yet enabled us to arrive at any conclusions regarding the structure of the colloidal particle. The phenomenon is too complicated; too many factors are playing a part. To analyse the nature of the electric double refraction, we should instead be guided by the phenomena in the magnetic field, where the disturbances are not so great.

---

* *Cf. l. c.*

† *Cf.* "On Accidental Double Refraction in Colloids," Upsala, 1924.

LXI. *An Oscillographic Study of Anodic Polarization.* By V. H. L. SEARLE, *M.Sc., Asst. Lecturer in Physics, Univ. College of the South-West of England*[*].

1. INTRODUCTION.

THE phenomenon of anodic polarization and its application to the rectification of alternating current have attracted the attention of many investigators, and the main features of the effect may now be considered to be well established although there are still differences of opinion as to its exact cause. In 1914 G. Schulze and R. Lindemann[†] put forward a view involving electronic processes in an exceedingly thin gas film on the surface of the valve metal. A short time later C. W. Greene[‡] carried out measurements on the counter e.m.f. at extremely small intervals of time after charging, and concluded that this back e.m.f. is alone sufficient to account for the current reduction. The results obtained seemed to be in accord with the gas film and ionic diffusion theories. It was also shown in the same year by G. Schulze[§] that total rectification does not occur, *i. e.* that the valve action is incomplete. A. L. Fitch[‖] in 1917 made potentiometer measurements of the counter e.m.f. with aluminium in saturated sodium phosphate solution. His results indicated that any method of experiment in which an appreciable time must elapse during the taking of data will introduce serious errors owing to changes occurring in the cell. In the same paper a theory was advanced of a double dielectric one part of which changes with the time of open circuit and the other with the time of closed circuit. F. Streintz[¶] traced a close similarity between this case and the unipolarity observed with crystals of sulphides and metals, and he concluded that the polarization appears to be partly galvanic and partly dielectric—the latter being due, according to G. Schulze, to a film of oxide and to gaseous oxygen in the film. Schulze[**] regarded the formed anode as a condenser of high capacity and resistance. The resistance of the oxide film layer is small compared with that of the gas layer, and the ohmic resistances are by no means constant. To investigate the completeness of rectification produced by the valve action of a formed anode, F. H. Newman* carried out an oscillographic study, using aluminium and nickel electrodes in dilute sulphuric acid, and it appeared from his results that rectification is complete within the limits of current measurement possible with an oscillograph record. Recently, J. A. Crowther and R. J. Stephenson† concluded that the high resistance of a polarized electrode is due entirely to a gas film.

---

[*] Communicated by Prof. F. H. Newman, D.Sc.

[†] *Phys. Zeitschr.* xv. p. 254 (1914).

[‡] Phys. Rev. iii. ser. 2, p. 264 (1914).

[§] *Archiv f. Electrot.* iii. p. 43 (1914).

[‖] Phys. Rev. ix. p. 15 (1917).

[¶] *Phys. Zeits.* xxi. p. 471 (1920).

[**] *Phys. Zeits.* xxii. p. 146 (1921).

2. EXPERIMENTAL.

The two main features of the polarization effect with which the present experiments are concerned are the rate of formation of the electrode by means of direct current and the degree of recovery of the cell following a cessation of the current. Incidentally both experiments test the completeness of polarization produced by the employed current densities, and give an indication of the effectiveness of an electrolytic rectifier at low alternation frequency.

For all the experiments the electrolyte used was a saturated solution of ammonium phosphate with a nickel cathode in combination with an anode of aluminium. The same cathode was used throughout, but the surface area of the anode was changed to effect an alteration in the current density. Although, in practice, the whole series of readings for a given size of anode was carried out before a change was made in the anode, it would be convenient here to describe the comparative results obtained for the same kind of experiment rather than for the same electrode.

In investigating the rate of formation of the anode, a simple time and current reading was taken. At a noted instant contact was made in a circuit containing a battery of about 20 volts, the electrolytic cell with an anode of new polished aluminium, and a large range milliammeter. The current value was noted every 5 seconds for the first minute, and then at greater intervals until a steady state was reached. The current was then left on for about 12 hours, to note any slow creep. The same experiment was later performed with another fresh anode of different surface area.

To investigate the power of recovery which the cell possesses when the current is switched off, some arrangement was required by means of which contact could be made after a definite recovery period, and at the same time current records could be made at exceedingly small time-intervals after the current recommenced to flow. The oscillograph offered a convenient means of doing this, and accordingly a device was made to ensure that, when the falling plate reached the slit in the fall tube, contact in the electrical circuit was just made and the initial current form was recorded as an oscillogram. From a measurement of the curves made by a tuning-fork circuit in a previous investigation [*], it was found that the plates fell in the camera with practically the same acceleration, which was only slightly less than that of free fall. This suggested the employment of a falling weight, released simultaneously with the plate, which should actuate a spring contact placed at the camera-slit level. The actual form of contact used comprised two steel springs carrying brass contact studs. These were normally kept from touching by a thin ebonite strip, which was mounted on one end of a rocking lever whose other end was depressed by the falling weight. This forced the ebonite from between the contact studs, and thus established the current. As a system of time coordinates the second vibrator of the oscillograph gave a trace of the tuning-fork current on the falling plate, as described in the previous paper [†]. The time of fall of the weight was known accurately and thus, since the time between the stoppage of the current and the release of the weight could be adjusted exactly, the whole interval during which no current flowed was known. To break the current at a noted time more exactly than could be done by the insertion of the ebonite strip between the contact studs, a key was placed in parallel with the latter and, with the strip in position for the falling weight, the recovery period began with the opening of the key.

---

* Phil. Mag. xlix. p. 1029 (1925).

§ Phil. Mag. xlix. p. 1066 (1925).

3. RESULTS.

(a) *Formation of Oxide Film.*

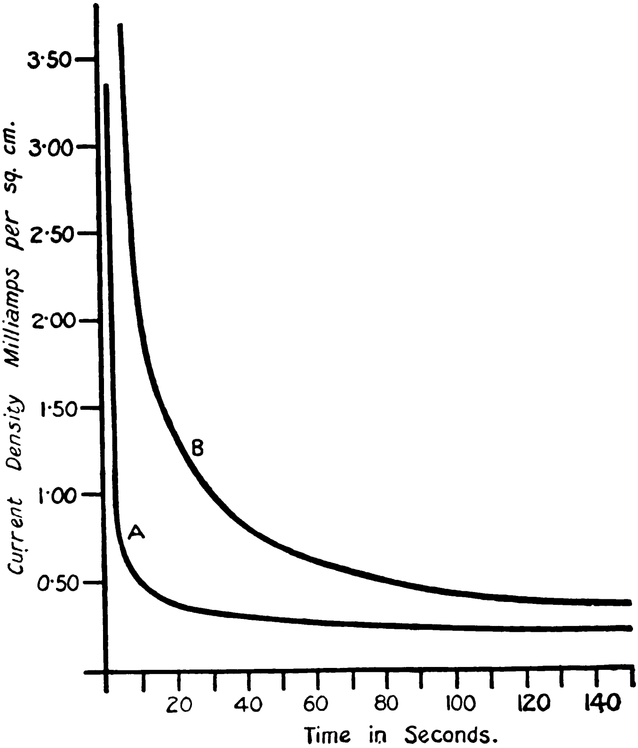
The connexion between current and time during the formation of the oxide film in the anode is shown in fig. 1. The curve A was obtained using an anode of surface area 140 sq. cms. with a battery of 18·6 volts, no resistance other than those of the electrolytic cell, the spring contact and the milliammeter being in the circuit. The rate of polarization is seen to be at first very rapid, since the current density was reduced to only twice its final small value—0·207 milliamps per sq. cm.—in about 11 seconds, while the final value was not attained until 180 seconds after making contact. This value was found to persist without change during the twelve hours' examination for any slow creeping effect. For the second experiment, the voltage was increased to 24·6 volts and the new anode surface area was 63 sq. cms. The resulting curve is shown at B, fig. 1,

---

[*] V. H. L. Searle, Phil. Mag. l. p. 738 (1926).

[†] *Loc. cit.*

Fig. 1.

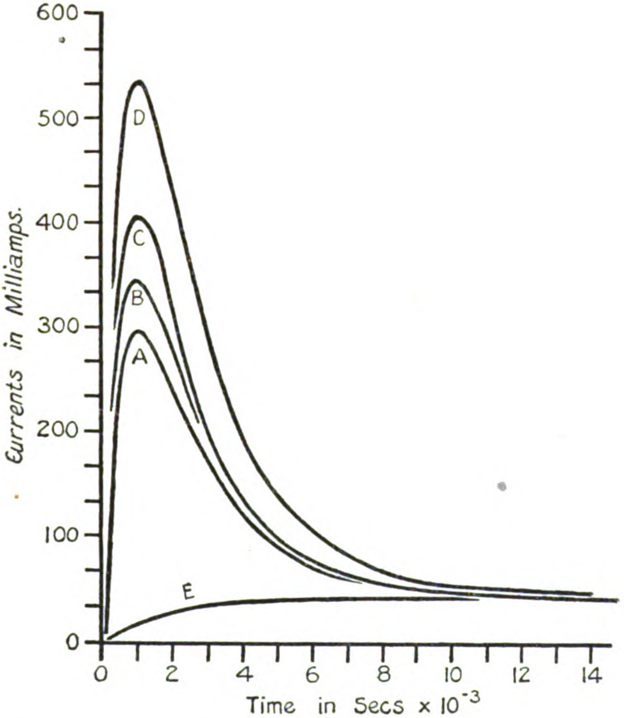


and it will be seen that the polarization effect in this case is less rapid, the time for the current to fall to twice its final value—0·159 milliamp. per sq. cm.—being now 145 seconds. In both cases no further change could be noticed in the current during twelve hours after the complete formation periods—3 mins. and 9 mins. respectively.

(b) *Depolarization Effect.*

Fig. 2 shows the result of the recovery which follows a cessation of the current after full oxide formation has recurred, and refers to the same anode as that of A, fig. 1. Curve A, fig. 2, was obtained from the oscillograph trace after the current had ceased for 1·5 secs. The other curves, B, C, and D of fig. 2, are the results of cutting off the current for 5·5, 15·0, and 30·0 secs. respectively. Curve E, fig. 2, indicates what would have been the result in all these cases if no depolarization followed current cessation. The method of arriving at this curve is indicated later.

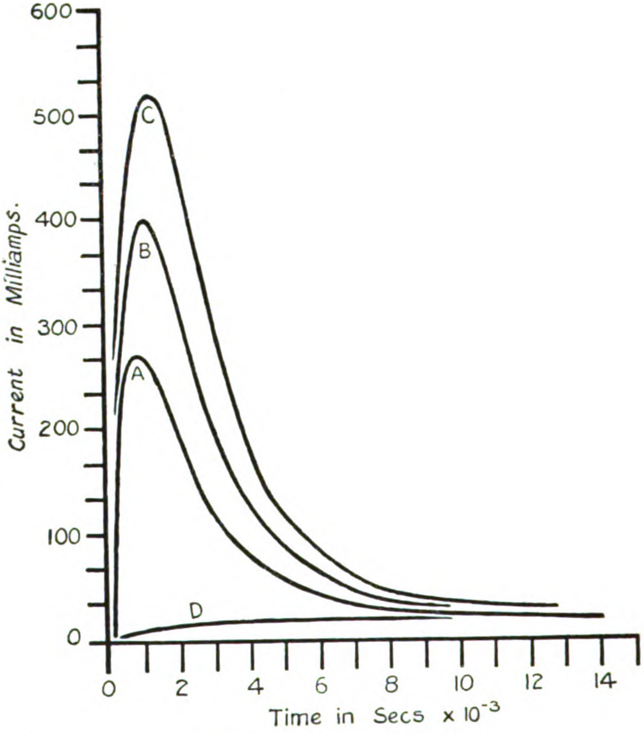
Fig. 2.



In fig. 3 similar graphs connecting current and time are shown for the anode of B, fig. 1. A, B, and C of fig. 3 refer to recovery periods of 30 sec., 3 mins., and 5 mins.

respectively, while D again shows, for comparative purposes, the curve for no depolarization.

Fig. 3.



4. Discussion of Results.

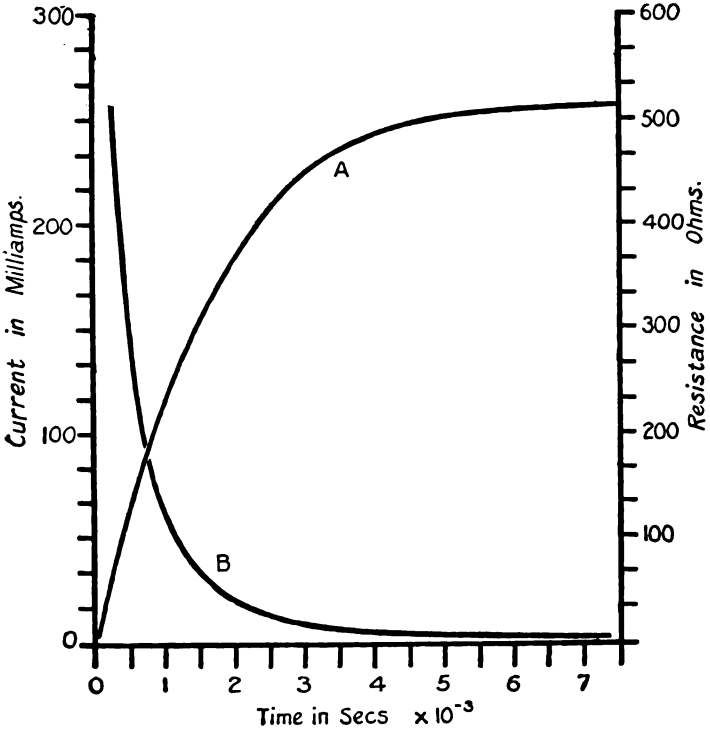
(a) *Formation of Anode.*

The first fact which becomes evident from a study of fig. 1 is the great rate of polarization, especially in the early stages of film formation, which occurs even in a previously polished aluminium surface. The result is the same as would have been obtained in the second series of experiments if the recovery had been complete, and the oscillograph curve would thus have had a very sharp peak. It would probably not be of very great value to modify the experiment to make an oscillograph record using a previously unformed anode, as the inertia of the moving system would prevent the mirror from following such a rapidly changing current. Comparison of the two curves shows a greatly lengthened time for steady conditions to be reached with increased voltage and decreased anode surface. Additionally, the fact that a steady state is reached before the current falls to zero is in accordance with the statement of G. Schulze * that the valve action is incomplete although, for small surface areas, the rectification may appear, as in the experiments of F. H. Newman †, to be perfect.

(b) *Depolarization Effect.*

As would be expected, the degree of recovery depends on the time for which the current has ceased. This is indicated by the progressive changes shown by the curves of either fig. 2 or fig. 3. It should be remembered, however, in studying these curves, that they are complicated by the time required for complete contact of the brass studs previously referred to. In order to investigate this factor, a separate record was obtained when the electrolytic cell was removed and contact was established in a circuit containing only a battery, the oscillator strip, and a non-inductive resistance. The result is shown in fig. 4, in which curve A gives the relation between time and current, while B associates time with the corresponding contact

Fig. 4.



---

* *Loc. cit.* † *Loc. cit.*

resistance. From A, fig. 4, the comparison curves E, fig. 2, and D, fig. 3, were obtained. By combining the results shown in fig. 4 with those of either fig. 2 or fig. 3, the variation of the ohmic resistance of the electrolytic cell with time may be obtained, but no great accuracy is possible since at the specially interesting time—the stage when contact is first re-established—the contact resistance is changing too rapidly for exact calculation.

The smooth curves of figs. 2 and 3 were not obtained in every case, but sometimes irregular serrations appeared, particularly during the early part of the polarization period. These were attributed to bubbles of oxygen leaving the anode surface and thus altering the electrolytic resistance to a comparatively large degree. Later, when polarization is practically complete, a single bubble of oxygen would not greatly affect the now large resistance. This result seems to support the view of J. A. Crowther and R. J. Stephenson* that the polarization is due entirely to the large resistance of the gas film.

5. SUMMARY.

1. The rate of formation of anodic films has been studied, and it has been found that the valve action is not complete.

2. The final steady current density measured in milliamps. per sq. cm. per volt increases as the anode surface area increases.

3. Rapid recovery accompanies a cutting off of the polarization current. This indicates that the rectification of slow alternations would be incomplete.

4. The resistance of such an anode seems to be due almost entirely to the gas film formed on it.

The author wishes to express his thanks to Prof. F. H. Newman for suggesting this investigation and for the interest taken in its course.

---

* *Loc. cit.*

LXII. *A New Method of obtaining a Luminous Discharge in Gases at very Low Pressures.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

MAY I call your attention to a paper of mine in the *Annal. d. Physik*, vol. lxxvii. p. 287 (1925), entitled "Ueber die Glimmentladung bei schnell wechselndem Feld," which covers the same subject as a recent interesting article (Phil. Mag. vol. ii. p. 129 (1926): "A New Method of obtaining a Luminous Discharge in Gases at very Low Pressures") by Messrs. E. W. Gill and R. H. Donaldson. These authors have measured the minimum potentials required to maintain a discharge in a gas at different pressures if oscillations of the order of $4 . 10^7$ per second are used. They find that the minimum potential decreases continuously as the pressure is reduced (to about 50 volts at a pressure $p < \frac{1}{100}$ mm. of mercury). The authors are evidently not aware of my paper, which contains a large number of careful measurements of these potentials, obtained by a method which is capable of giving far more accurate results than the one which they employed. (My method involves the measurement of the deflexion of an independent cathode stream in a high vacuum.) The curves which I obtained show without doubt that the continuous decrease of the minimum potential with pressure obtained by the authors is solely caused by mercury vapour from the Toepler pump, which they evidently did not prevent from reaching the discharge-tube; and that the minimum potential rises again at a pressure of a few thousandths of a mm., if the mercury vapour is kept away. Moreover, I employed the "Continuous-flow" method of W. Wien, which eliminates perfectly the impurities that are always set free in a gaseous discharge.

May I also mention that the lowest potential with which I could maintain a discharge between cold electrodes, in neon gas for example, was 15 volts (lower than the ionizing potential).

Yours faithfully,

Dr. FRITZ KIRCHNER.

München,
August 12, 1926.

LXIII. *A New Method of obtaining a Luminous Discharge in Gases at very Low Pressures.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

PROFESSOR KIRCHNER has very kindly sent us a copy of his letter to you and we should like to express our regret that we had not previously seen his paper. We agree with him that the discharges we obtained with very low voltages were due to mercury vapour, in fact, we stated this specifically in our paper, and it is also evident that the potential must reach a minimum as the pressure is reduced, as no discharge could pass through an absolute vacuum.

We do not agree, however, that the deflexion of a cathode stream gives far more accurate measurements of alternating potentials than our method. Our method is capable of the greatest accuracy if the alternations are not too rapid, and it only becomes less accurate when the time of an oscillation is comparable to the time the electrons take to cross the measuring instrument; a limitation which applies equally to the cathode stream instrument. In addition, the latter only measures the electric force, while we measured the actual potential between the electrodes. When the discharge is passing the electric force is not uniform.

Yours faithfully,
E. W. B. GILL,
R. H. DONALDSON.

Merton College,
Oxford.

LXIV *The Water-Spark Absorption Spectrum of Iron.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I REGRET that I overlooked the paper on "Spèctres d'étincelle dans l'eau" by M. Léon Bloch and Eugène Bloch. However, I may be permitted to point out that the object of my work on the water-spark absorption spectrum of iron was to eliminate the more fundamental lines of the arc-spectrum of iron, and thus to elicit information about the utility of this method as an aid to the classification of the spectra of more refractory elements, of which the absorption spectra cannot be readily studied by the usual method; I have pointed out that by modifying the experimental conditions, the "*d*" and "F^1" levels of the iron atom can be separated.

Yours faithfully,
A. K. Sur.

Allahabad.
8 April, 1926.

LXV. *A New Method of Producing a Discharge in Hydrogen.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In claiming in the July issue of your Magazine to describe a new method of producing a discharge in hydrogen, Messrs. E. W. B. Gill and R. H. Donaldson would appear to be unaware of earlier researches dealing with the production of discharges in gases at frequencies of the order 10^7 cycles per second [*]. In a recent communication to your Magazine, data have been given characterizing the discharge in hydrogen at the frequency $1{\cdot}5 \times 10^7$ cycles per second [†]. These data indicated that the fields sustaining ionization by collision were considerably smaller than those necessary when using alternating potentials of commercial frequencies. Experiments were therefore commenced, and are now in progress, to determine the variation of dielectric strength of hydrogen and other gases with the frequency of the alternating potential applied to produce the discharge. It is anticipated that it will be possible soon to communicate the results which have been obtained.

Yours faithfully,

R. Winstanley Lunt, M.Sc., Ph.D.

The William Ramsay Laboratories
of Physical and Inorganic Chemistry,
University College, London.
July 23, 1926.

[*] Lunt, Proc. Roy. Soc. A, cviii. p. 172 (1925).
[†] Lunt. Phil. Mag. xlix. p. 1238 (1925).

LXVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. i. p. 896.]

January 6th, 1926.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

THE following communication was read:—

'The Geology of the Suk Hills (Kenya Colony).' By Vincent G. Glenday, M.A., F.G.S., and John Parkinson, M.A., Sc.D., F.G.S.

The Suk Hills lie in the northern part of Kenya Colony, midway between Mount Elgon and the southern half of Lake Rudolf. Sekerr, their highest point, reaches an elevation of nearly 11,000 feet. So far as the authors are aware, this country hitherto has been geologically almost unknown. It is described by a southern traverse north of the Trans-Nzoia Escarpment to the Kerio River; and by a northern, including part of the Swam River and the Turkwal Gorge.

With insignificant exceptions, the rocks are of Eozoic age, and fall into two groups: a series of completely metamorphosed sediments, probably including ashes, and microcline-orthogneisses. As elsewhere, the former includes crystalline limestones, quartz-schists, kyanite-schists, garnet-mica-schists, and the like. After petrographical descriptions of the principal rock-types, the senior author concludes that the former group so closely resembles the Turoka Series from the border of Tanganyika Territory that they cannot be separated, the whole being contemporaneous in general terms. The strike of the planes of foliation of the Suk schists characteristically varies little from north and south. If the further conclusion is correct, that, of the two groups, the second is intrusive into the first, the relationship becomes of considerable importance, owing to the large area formed by these or closely similar rocks.

January 20th, 1926.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

The following communication was read:—

'The Stratigraphy and Structure of the Cambrian Slate-Belt of Nantlle (Carnarvonshire).' By Thomas Owen Morris, B.Sc., and Prof. William George Fearnsides, M.A., F.G.S.

This paper describes the results obtained by mapping, on the 6-inch and 25-inch scales, the rocks and structures exposed over about 10 square miles of the slate-quarrying district of Llanllyfni, Tal-y-sarn, Nantlle, and Moel Tryfan, in Carnarvonshire.

Stratigraphy.

The Nantlle Slate-Belt is the south-western part of the outcrop of the Cambrian rocks of Northern Carnarvonshire, which rest with appreciable unconformity upon the late pre-Cambrian volcanic rocks running south-westwards from Llanberis. The following succession has been established by the mapping, and is constant in all its divisions along the length and strike of the district:—

ORDOVICIAN.	**Dark Slate Group**; including some part of the zone of *Didymograptus murchisoni*.	

Strike-Fault.

		Thickness in feet.
UPPER CAMBRIAN.	**Cymffyrch Grit Group**; coarse grits with mudstone-beds	600
MIDDLE CAMBRIAN.	**Green Slate Group**; green, greenish-blue, and light-brown slates, yielding *Hyolithus*	300
	Mottled Blue Slate Group; upper part: smooth silky-red slates; lower part: purple slates splashed with irregular green patches	600
	Pen-y-Bryn Grit Group; coarse massive grits.	200
	Striped Blue Slate Group; stripes most abundant in the uppermost and in the lowest parts, which have a purplish tinge; stripes well-banded and generally fine-grained	600
	Dorothea Grit Group; coarse thickly-bedded grits, with intercalated thinly-bedded white and green banded silts	100
	Purple Slate Group; the upper part has a characteristic red portion, with abundant green spots; green stripes of coarse grit are most abundant in the highest and in a middle part of the group	800
LOWER CAMBRIAN.	**Glog Grit Group**; coarse grits, with intercalated beds of mudstone, quartzite, and conglomerate	2000
	Cilgwyn Conglomerate; conglomerate, with pebbles measuring up to 6 inches in length in a coarse grit-matrix	500
PRE-CAMBRIAN.	**Tryfan Grit Group**; upper part: finely banded green and white silt-rocks; lower part: coarse grits and felspathic tuffs	900
	Clogwyn Volcanic Group; rhyolitic and andesitic lavas and tuffs	1000

A correlation of these rocks with equivalent rocks in Southern Carnarvonshire and Merioneth is suggested. It is argued that the Lower Cambrian sediments are land-waste from the pre-Cambrian rocks of North-Western Carnarvonshire and Anglesey, whereas the later Middle and Upper Cambrian material was brought in from an unknown source away to the east and south. Ordovician sediments are faulted against the basal member of the Upper Cambrian. A buttress of Ordovician volcanic rocks flanks the Nantlle area on the south-east side; but, within the area mapped, there are only altered dolerite-dykes, later than most of the impressed structures, to represent (and that a very late stage in) the cycle of Ordovician-Devonian igneous activity.

Structure.

The Nantlle district was deeply involved in the making of the Devonian alpine range, the basal wreck of which is now Snowdonia, and all sedimentary material within the Slate-Belt was compelled to fold, and then to crush until, both in bulk and in detail, it began to shear and creep. The importance of progressive movement in the development of cleavage is emphasized. Cleavage in the Nantlle Slate-Belt is almost vertical. Many folds have associated with them vertical strike-faults or slides, which, by tearing the middle limbs, have increased the vertical displacement. Often stronger beds are rolled out or packed as lenticles along surfaces of slip which behave as thrust-planes. Strong rocks rise on the north-western face of each slide, bend over, and are cut off by the next slide towards the north-west. The total displacement across individual slides, measured stratigraphically, may amount to many hundreds of feet. More boundaries of slate 'veins' and quarry properties are determined by slides than by bedding-planes. Between slides the slate-beds have characteristic anticlinal structures, the synclines being suppressed. Some slides are evident surfaces of discontinuity, but the movement along many slides was prior to the completion of growth of authigenic minerals, and, as along cleavage-planes, these surfaces of slip are sealed. The scale and frequency of the folding at Nantlle is comparable with that in the mining district of Wanlockhead. The slide-blocks are longer and narrower than the strike-fault strips between Caermarthen and St. Clears; but secondary thrusting is impersistent, and not as orderly as in the schuppen which affect the Cambrian rocks of the North-West Highlands.

With removal of load by denudation, joints and other tensional fractures have appeared. The direction of some of these is related to rock-texture, but bevels, etc. cross them at acute angles. The latest cross-faults are master-fractures, which traverse all other structures as also the pre- and post-Cambrian formations that flank the Slate-Belt. The direction of these is north of north-west, as the geometry of the half-dozen which cross the quarry-region suggests that block-movement was associated with northward shift on the eastern side of each. Most of the dolerite-dykes follow bevels, and two have been intruded along the latest cross-faults.

A petrographic description of the pre-Cambrian rhyolites and of a hornblende-andesite is given, with chemical analyses. Petrographic evidence also establishes the existence of secondary (authigenic) micaceous minerals with or without recrystallized quartz in all the rocks of the Slate-Belt, and especially in those slates which are of greatest economic value. New-formed bladed chlorite is abundant in the Cambrian grits, and some of it is passing into biotite. Authigenic tourmaline in minute long prisms is a frequent constituent of both coarse and fine felspathic sediments throughout the Nantlle Slate-Belt.

February 3rd, 1926.—Dr. J. W. Evans, C.B.E., F.R.S.,
President, in the Chair.

Prof. S. James Shand, D.Sc., F.G.S., delivered a lecture on the Alkaline Rocks and Ring-Intrusions of Pilansberg (Transvaal), illustrated by specimens, diagrams, and lantern-slides.

He said that Pilansberg, a group of hills in the Western Transvaal, is the largest of the secondary eruptive complexes which are superimposed upon the great complex of the Bushveld. The energy which caused the extrusion of the Bushveld felsites, and the intrusion of the sheets of norite and red granite, was not quite exhausted by these tremendous events; but reactions went on underground, which led to the opening of new channels through which alkaline magma ascended. Plugs and dykes of syenite and foyaite cut the granite and the norite in Sekukuniland, in the Pretoria district (Franspoort, Leeuwfontein, etc.), and in the west, where Pilansberg presents one of the greatest intrusions of purely alkaline rocks in the world. The Berg is circular in outline, and covers about 200 square miles. The rocks may be grouped into (1) a volcanic series and (2) an intrusive series. The former includes felsites, phonolites, tinguaite, and a great development of tuff and breccia; these rocks formed a cover under which the intrusive series crystallized. The removal of most of the cover has laid bare the underlying foyaites and syenites, which are arranged in concentric rings, as follows:—(1) a core of pseudonepheline-syenite; (2) a ring of white granitic foyaite; (3) a ring of green porphyritic foyaite; (4) a half-ring of tinguaite; (5) another ring of white foyaite; and (6) a ring of red syenite. The principal problems presented by the Berg are the cause of this remarkable structure, and the origin and method of emplacement of the alkaline rocks.

February 19th, 1926.—Dr. John William Evans, C.B.E., F.R.S., President, in the Chair.

The President delivered his Anniversary Address dealing with the subject of Regions of Compression.

He said that the characteristic structures of regions of compression—that is to say: folding, thrust-faulting and slaty cleavage—are, as a rule, the result of horizontal forces ultimately to be attributed to the contraction of the Earth's interior as it cools. It has been doubted whether, with the energy released by radioactive elements, the Earth cools at all. It is certain, however, that the whole of that energy is not converted into heat; much must be employed in effecting physical, chemical, or atomic changes in the surrounding rock. The substance of the ionized pleochroic haloes in biotite-mica is hundreds of thousands of times greater than the radioactive material in the zircon round which they are formed, and they must represent a relatively enormous absorption of energy.

Dr. H. Jeffreys shows that the contraction on cooling of the crystallized rocks is more than enough to account for the folding of existing mountains. But there are many folds of ancient mountains, now worn down, which would require still more contraction. This may have occurred in the following ways: (1) the contraction of uncrystallized magma retaining the volatile constituents is greater than that of crystallized rocks; (2) the contraction on crystallization is equal to that on a fall of temperature of very many degrees; (3) contraction may take place on changes of crystal-structure, chemical composition, or even atomic nature; (4) contraction will result from the loss of volatile constituents; (5) it must also follow on the increase of pressure in the Earth's interior due to the slowing-down of its rotation. On the other hand, the extent of the crust may be locally increased in periods of tension by (1) infilling of rifts by igneous intrusions, and (2) slip-faulting; and also by hydration of rocks.

Compression and folding may also result (1) from change in the Earth's form on diminished rotation; (2) from change in the position of the crust relatively to (*a*) the poles and equator, (*b*) the maximum of gravitational force.

In illustration of the process of folding, two examples are described: (1) the 'Hercynian,' or 'Armorican,' folding of the south-western peninsula of England and South Wales; and (2) the Wealden folding between the Thames Valley and the 'Massif Central' of France. In the former case it is shown that the accumulations of sediments from mountains formed by Caledonian movements resulted in a 'sedimentation-subsidence.' This was slightly contracted and deepened by early Hercynian compression.

This 'compression-subsidence' allowed still greater accumulations of sediments. The oncoming of the main Hercynian compression contracted much more vigorously the basin of subsidence, forcing up the contained sediments into folds. The accumulated weight of these gave rise to a deep 'folding-subsidence.' A distinction is made between the exterior structure formed from the old floor of deposition and the interior structure consisting of the sediments deposited on it. The outflow of the plastic 'sima' from below the deepened basin raised its southern rim, with the result that in the course of the compression the folds were tilted northwards and dipped southwards. The folds are defined by the calcareous and arenaceous banding, while the argillaceous material between flowed rather than folded; and it is this flow which is now represented by slaty cleavage. In a later stage, both outer and inner structures were traversed by thrusts, which, like the folds and cleavage, dipped southwards. The greatest of these thrusts brought, in the extreme south, the pre-Cambrian rocks up against the Palæozoic. In the south of Devon and Cornwall this and other thrusts drove older rocks over new; but in North Devon new were brought over old. The displacement of the 'sima' in the course of mountain-building resulted in the intrusion of basic magmas, while the granites were probably derived from a reservoir beneath the uplifted pre-Cambrian rocks on the south.

The Wealden folding had its origin in sedimentary accumulations in a vast Triassic plain paved with the eroded outcrops of older rocks, and bordered by Hercynian highlands. The sedimentation-subsidence was widespread, and the compression in late Secondary and Tertiary times deepened it considerably, so that its floor has never been reached by borings south of the northern slope of the Wealden anticline, except in the neighbourhood of the Massif Central and the Hercynian tracts on the east and west. The actual compression in this region was small compared with that which occurred about the same time in the Pyrenees and in the Alps, but it threw the sediments of the interior structure into numerous folds.

A brief comparison was made between the great earth-movements of the Alps and those which formed the subject of the Address.

February 24th, 1926.—Dr. F. A. Bather, M.A., F.R.S.,
President, in the Chair.

The following communication was read:—

'The Geological Structure of Ben Lawers and Meall Corranaich (Perthshire).' By Gertrude Lilian Elles, M.B.E., D.Sc., F.G.S.

The country dealt with lies between Loch Tay on the south and Glen Lyon on the north, and between the Loch Tay Fault on the east and the Ericht-Laidon-Tyndrum Fault on the west. Evidence is brought forward to show that the line of junction between the Ben Lui Schists and the Ben Lawers Schists is a mechanical one of the nature of a folded slide, the Ben Lawers Slide, the rocks above this slide constituting a veritable nappe, the Ben Lawers Nappe. The structure of the rocks composing this nappe is dealt with in some detail, and it is shown that the metamorphic condition of the rocks indicates that the folding now exhibited by them is a relatively late feature of the structural story, and obscures their original relationships, which seem to demand inversion of the beds on a large scale such as would be brought about by recumbent folding.

March 10th, 1926.—Dr. F. A. Bather, F.R.S., President. in the Chair.

The following communication was read:—

'The Pleistocene Deposits of the Lower Part of the Great Ouse Basin'. By Prof. John Edward Marr, Sc.D., F.R.S., For.Sec.G.S.

In a paper published in the Society's Journal (vol. lxxv, 1919–20, p. 204) the author described the Pleistocene deposits in the immediate vicinity of Cambridge.

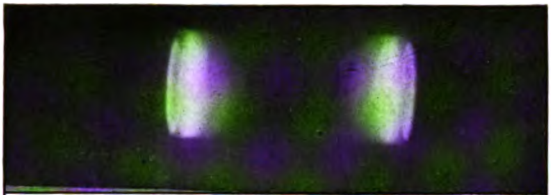
In the present paper a wider area is described. The results, in the main, confirm the conclusions of the previous paper.

It is argued that a period of aggradation in Lower Palæolithic times intervened between two periods of glaciation of the district, and that, subsequently to the second glaciation, erosion occurred, with minor periods of aggradation in Upper Palæolithic times.

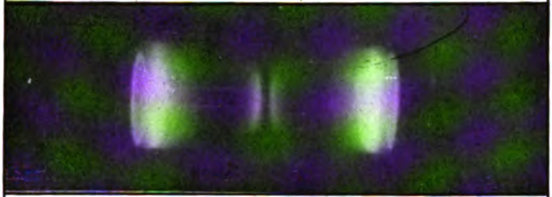
The author also discusses the general character of the river-diversions which occurred in the district in Pleistocene times.

An Appendix by Mr. A. S. Kennard & Mr. B. B. Woodward deals with the non-marine mollusca.

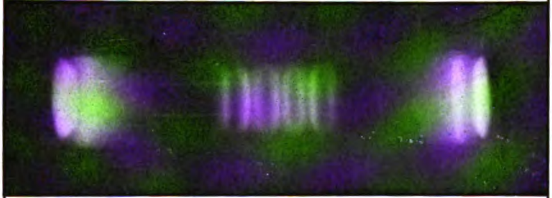
[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]



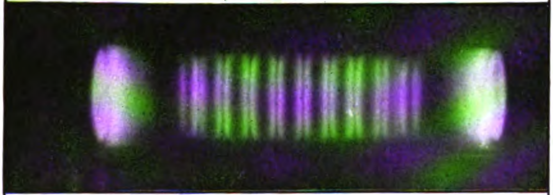
No. i



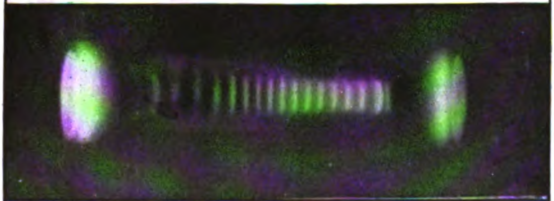
No. ii



No. iii



No. iv



No. v.

Fig. 1.

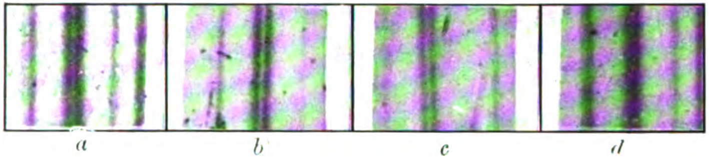


Fig. 2.

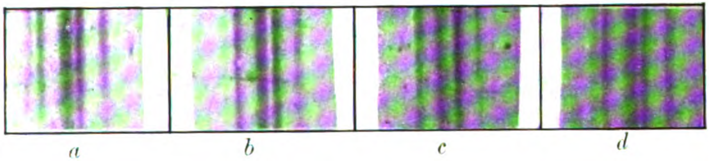


Fig. 3.

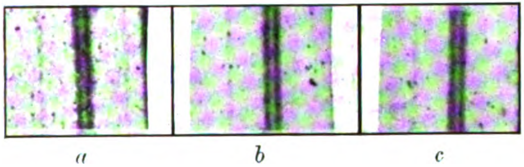


Fig. 4.

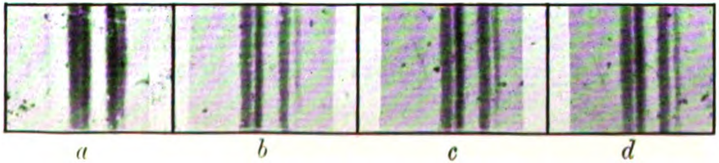


Fig. 5.

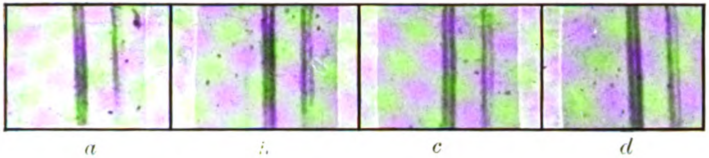


Fig. 9.

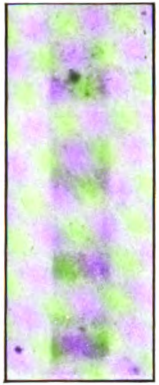


Fig. 6.

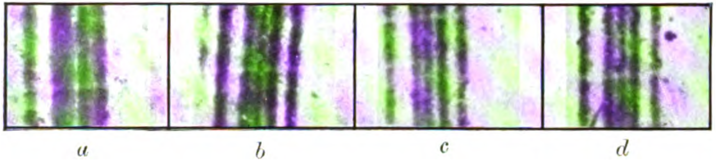


Fig. 7.

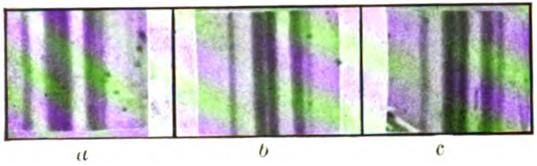
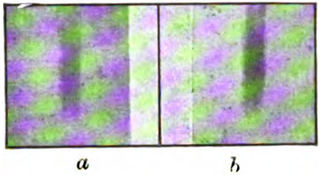
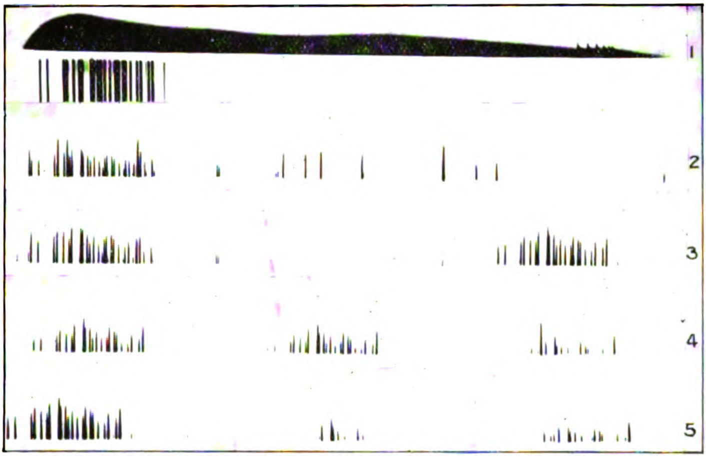
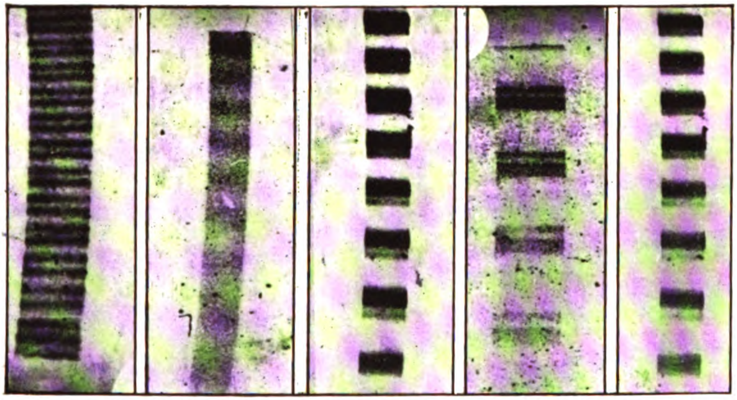


Fig. 8.




1
2
3
4
5



1. Cd. 2288. Thin Plate. .000.
2. ,, ,, Thick ,, ·021 (or −·017).
3. ,, 3261. Thin Plate. ·000 (10).
4. ,, ,, ,, ,, Main Comp. reversed. −·019 (2).
4. ,, ,, Thick Plate.

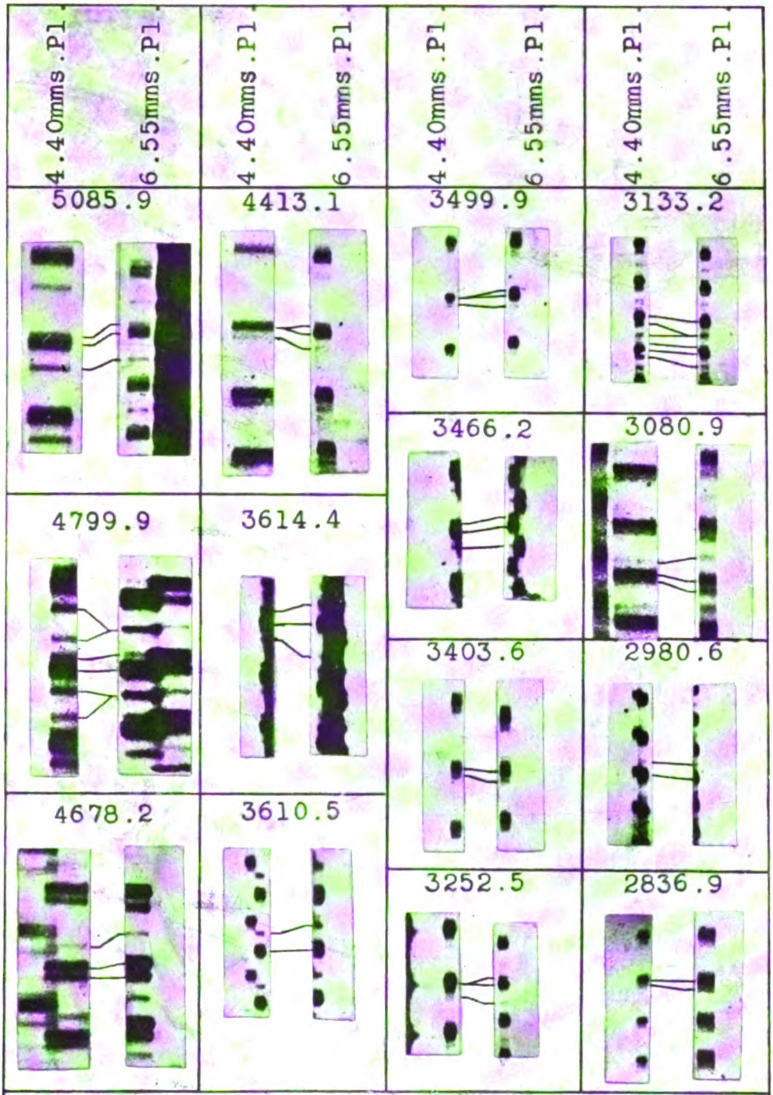
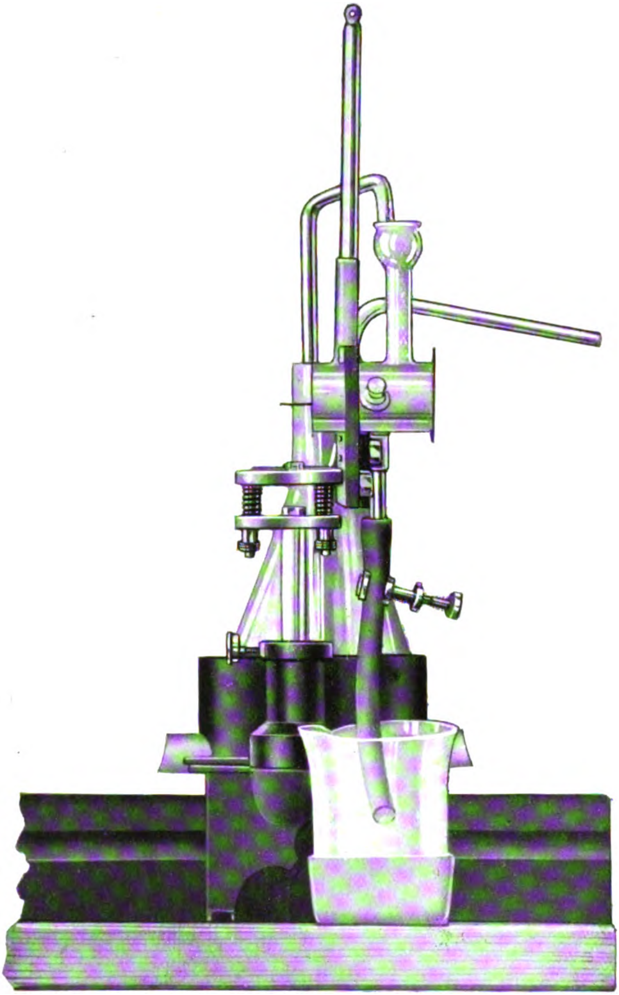


Fig. 2
Fine Structure of Cd. Lines.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

OCTOBER 1926.

✓

LXVII. *The Theory of the "Boys" type of Double Resonator* [*].

By E. T. PARIS, *D.Sc.*, *F.Inst.P.*[†]

§ 1. *Introduction.*

THE "Boys" type of double resonator is used in the construction of sensitive sound-receiving instruments, and consists of a resonator of the "stopped-pipe" variety combined with one of the Helmholtz pattern.

As used for sound-reception the resonator is combined with some form of detector, for example, a Rayleigh disk or a "hot-wire" grid. The detector is mounted in the orifice of the Helmholtz resonator and the magnitude of its response (angular rotation in the case of the Rayleigh disk, and change of electrical resistance in the case of the "hot-wire" grid) provides a measure of the amplitude of the oscillatory air-current in the orifice, and hence of the pressure-amplitude in the original sound-wave.

The function of the double resonator is to magnify the vibrations occurring in the sound-wave so that they may be easily recorded by the detector.

By means of the detector the properties of the double resonator can be investigated experimentally, and, by plotting the response of the detector against the frequency of the sound stimulating the resonator, curves are obtained which exhibit characteristic double resonance features. Examples of these curves and methods for calculating the resonance-frequencies from the dimensions of the component resonators have been given in previous papers [*].

---

[*] The work described in this paper was carried out in the Acoustical Section of the Air Defence Experimental Establishment, Woolwich, with the assistance of the contribution made to the funds of the Section by the Department of Scientific and Industrial Research on the recommendation of their Physics Research Board.

[†] Communicated by Prof. Alfred W. Porter, D.Sc., F.R.S.

In this earlier work no allowance was made for any loss of sound-energy from the resonator. Such a loss must, however, always occur owing to the dissipation of sound into heat by the action of viscous forces in the narrow parts of the resonator and to the escape of sound from the mouth of the resonator into the surrounding air.

In the present paper, therefore, an attempt is made to develop a more complete theory of this type of resonator than has yet been given, allowance being made for the loss of sound-energy from both the causes just mentioned. It is clear from the form of the resonator that viscosity losses will be mainly confined to the narrow neck leading into the Helmholtz resonator. The motion in this neck is accordingly supposed to be resisted by a force proportional to the air-current passing through it.

It is convenient to approach the theory of the Boys resonator through that of the simple stopped pipe. A short account of the theory of the pipe is therefore given in § 2, and the theory of the Boys resonator is afterwards developed in § 3.

By way of illustration of the application of the equations obtained some numerical results are given in § 4, and confirmatory experiments are given in § 5.

§ 2. *The Theory of the Stopped-pipe Resonator.*

The behaviour of a stopped pipe under the influence of an external source of sound has been discussed by Helmholtz [†] and Rayleigh [‡]. The difficulty of the investigation lies mainly in the determination of that part of the velocity-potential inside the pipe which is necessary to allow for the escape of sound-energy from the open end, and a satisfactory solution has been obtained only in the case when the diameter of the pipe is small compared with the wave-length of the sound, so that the escaping sound-waves may be assumed to spread spherically from the centre of the mouth. This condition is sufficiently fulfilled in the case of Boys resonators as ordinarily made, since the diameters of the pipes commonly used are only from 1/10 to 1/20 of a wave-length.

---

[*] Proc. Roy. Soc. A, vol. ci. pp. 393-402 (1922), and Phil. Mag. vol. xlviii. pp. 770-783 (1924).

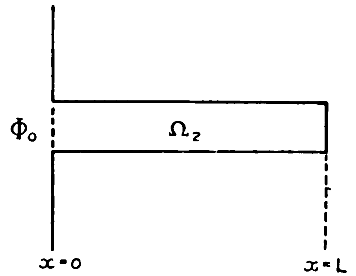
[†] Helmholtz's theory is given in 'Vorlesungen über theoretische Physik,' vol. iii. pp. 209-231 (Leipzig, 1898). The investigation originally appeared in Crelle's Journal (1859).

[‡] 'Theory of Sound,' vol. ii. (2nd ed.) p. 207.

It will be supposed that the mouth of the pipe is provided with an infinite plane reflecting flange, so that the difficulty of making allowance for the scattering of sound from the external surface of the resonator is avoided. So far as the present problem is concerned the principal effect of removing this flange would be to increase the rate at which sound-energy escapes from the open end.

Let the pipe lie with its mouth in the y, z plane (fig. 1) with its axis parallel to the axis of x.

Fig. 1.



A plane wave, $A\epsilon^{\iota k(at+x)}$, travelling from within the pipe towards the open end, will suffer reflexion at the open end (where part of its energy will be transferred to the outside air) and will give rise to a reflected wave, $\beta A\epsilon^{\iota k(at-x)}$, where β is in general complex. The amplitude of the reflected wave is $|\beta|$, and if β_1 and β_2 are the real and imaginary parts of β respectively, the change of phase at reflexion is $\tan^{-1}(\beta_2/\beta_1)$. The form of the potential inside the pipe, necessary to allow for the escape of sound from the open end, is therefore

$$\Omega_1 = A(\epsilon^{\iota kx} + \beta\epsilon^{-\iota kx})\,\epsilon^{\iota kat}. \quad . \quad . \quad . \quad (2.1)$$

To Ω_1 may be added any stationary potential Ω_2, of the form $C\cos kx$, which may be necessary to balance the pressures due to external sources in the plane $x=0$. Thus, suppose that the potential Φ_0, at the mouth of the pipe, is due to a plane wave $F\epsilon^{\iota k(at-x)}$, then $C=2F$ and

$$\Omega_2 = 2F\cos kx\,.\,\epsilon^{\iota kat}. \quad . \quad . \quad . \quad . \quad (2.2)$$

The total potential inside the pipe is then—

$$\begin{aligned}\Omega_{12} &= \Omega_1+\Omega_2\\ &= \{A(\epsilon^{\iota kx}+\beta\epsilon^{-\iota kx})+2F\cos kx\}\,\epsilon^{\iota kat}\\ &= \{(F+A)\epsilon^{\iota kx}+(F+\beta A)\epsilon^{-\iota kx}\}\,\epsilon^{\iota kat}, \qquad . \quad (2.3)\end{aligned}$$

representing two plane waves of amplitudes $|F+A|$ and $|F+\beta A|$ travelling in the directions x-negative and x-positive respectively. The relative amplitudes and phases of the two waves must be adjusted—by a suitable choice of the complex constant A—so that the requirements of the problem are fulfilled in those parts of the pipe away from the mouth. Thus, when the pipe is closed at $x=L$, the following condition must be fulfilled:

$$\left(\frac{\partial\Omega_{12}}{\partial x}\right)_{x=L}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.4)$$

Whence, from (2.3),

$$(F+A)\epsilon^{\iota kL}=(F+\beta A)\epsilon^{-\iota kL}, . \quad . \quad . \quad (2.41)$$

so that

$$A=-\frac{2\iota\sin kL}{\epsilon^{\iota kL}-\beta\epsilon^{-\iota kL}}F. \quad . \quad . \quad . \quad (2.42)$$

The potential inside the pipe is therefore

$$\begin{aligned}\Omega_{12} &= 2F\left\{\cos kx-\frac{\iota\sin kL}{\epsilon^{\iota kL}-\beta\epsilon^{-\iota kL}}(\epsilon^{\iota kx}+\beta\epsilon^{-\iota kx})\right\}\epsilon^{\iota kat}\\ &= \frac{2(\beta-1)F}{\beta\epsilon^{-\iota kL}-\epsilon^{\iota kL}}\cos k(x-L)\,.\,\epsilon^{\iota kat}, \quad . \quad . \quad . \quad . \quad (2.5)\end{aligned}$$

indicating, as would be expected, a condition of stationary vibration, the positions of maximum pressure variation alternating with those of maximum velocity at distances of one-quarter of a wave-length.

The quantity denoted by β in the above equation is of frequent occurrence in acoustical problems. In all questions relating to the use of pipes as resonators, allowance must be made for the escape of energy from an open or partially open end, and β enters into the expression for the potential within the pipe. The method of calculating β in a particular case is dealt with below.

Let χ be the potential of the hemispherical sound-waves spreading from the mouth of the pipe, by means of which sound-energy is carried from the pipe into the surrounding medium.

If S_1 be an equipotential surface inside the pipe in the region of plane waves, taken as near to the mouth as possible, and S_2 be a hemispherical surface drawn outside the pipe with radius r as small as possible, compatible with the condition that the potential χ is the same at all points on S_2, then between S_1 and S_2 the transition will take place from plane waves (Ω_1) inside the pipe to the diverging hemispherical waves (χ) outside the pipe. The problem of finding the relation between Ω_1 and χ, which is essentially that of determining β, has been dealt with by Helmholtz (*loc. cit. supr.*) and Rayleigh [*]. Their methods, however, differed considerably. Helmholtz assumed the existence of a potential satisfying the general equation of wave-motion in the transition region between S_1 and S_2, and proceeded to find the relation between Ω_1 and χ by several applications of his extended form of Green's theorem. Rayleigh's method, which will be adopted here, is much shorter and proceeds on the assumption that, on account of the smallness of the dimensions (compared with the wave-length) of the region between S_1 and S_2, the motion of the air in this part of the pipe can be treated as that of an incompressible fluid. The conditions to be satisfied in the transition region are then: (*a*) that the total current across S_1 at any instant must be equal to the total current across S_2, and (*b*) that the total current through the transition region must be proportional to the difference between the velocity-potentials at S_1 and S_2.

If the disturbing potential Φ_0 is due to a pure tone of wave-length $\lambda\ (=2\pi/k)$, the most general form for χ will be

$$\chi = \frac{G}{kr}\epsilon^{ik(at-r)}, \quad . \quad . \quad . \quad . \quad . \quad (2.6)$$

where r is measured from the centre of the mouth, and G is independent of the space coordinates.

Conditions (*a*) and (*b*) can be expressed by the following equations:

$$\sigma\left(\frac{\partial\Omega_1}{\partial x}\right)_{kx\to 0} = \left(-2\pi r^2\frac{\partial\chi}{\partial r}\right)_{kr\to 0}, \quad . \quad . \quad . \quad (2.71)$$

$$\sigma\left(\frac{\partial\Omega_1}{\partial x}\right)_{kx\to 0} = c_0\left\{(\Omega_1)_{kx\to 0}-(\chi)_{kr\to 0}\right\}, \quad (2.72)$$

where σ is the cross-sectional area of the pipe, and c_0 is the conductance (hydrodynamical) of that part of the pipe lying between the surfaces S_1 and S_2. By substituting in (2.71) and (2.72) the values of Ω_1 and χ given in (2.1) and (2.6) respectively, we find

---

[*] 'Theory of Sound,' vol. ii. pp. 198–201.

$$\iota k\sigma A(1-\beta)=\frac{2\pi G}{k}=c_0\left\{A(1+\beta)-\frac{G\epsilon^{-\iota kr}}{kr}\right\}. \quad (2.8)$$

By elimination of G, this gives

$$\frac{1+\beta}{1-\beta}=\iota k\sigma\left(\frac{1}{c_0}+\frac{\epsilon^{-\iota kr}}{2\pi r}\right).$$

Since kr is small compared with unity,

$$\frac{1+\beta}{1-\beta}=\iota k\sigma\left(\frac{1}{c_0}+\frac{1}{2\pi r}-\frac{\iota k}{2\pi}\right). \quad . \quad . \quad (2.81)$$

So that

$$\beta=-\frac{1-\iota k\sigma\left(\frac{1}{c_0}+\frac{1}{2\pi r}-\frac{\iota k}{2\pi}\right)}{1+\iota k\sigma\left(\frac{1}{c_0}+\frac{1}{2\pi r}-\frac{\iota k}{2\pi}\right)}. \quad . \quad . \quad (2.9)$$

In this equation r is the radius of the hemispherical equipotential surface S_2. Since the diameter of the mouth is small compared with the wave-length, we may, following Rayleigh *, ignore the term $\frac{1}{2\pi r}$ in comparison with $\frac{1}{c_0}$. In this case, we have as an approximation:

$$\beta=-\frac{1-\iota k\sigma\left(\frac{1}{c_0}-\frac{\iota k}{2\pi}\right)}{1+\iota k\sigma\left(\frac{1}{c_0}-\frac{\iota k}{2\pi}\right)}. \quad . \quad . \quad . \quad (2.91)$$

In order to find a numerical value for β in any particular case it is necessary to assign a numerical value to c_0, the conductance of the mouth of the pipe. If the mouth is restricted the calculation of c_0 presents no difficulty, but if it is not restricted there appears to be no method by which a direct calculation of this quantity can be made. An estimate of its value in the case of a pipe of circular cross-section can, however, be made indirectly as follows.

Let the value of β given in (2.91) be inserted in (2.5). Then, after some reduction, the expression for the potential

---

* 'Theory of Sound,' vol. ii. p. 199.

inside the pipe becomes

$$\Omega_{12} = \frac{2\mathrm{F}}{\cos k\mathrm{L} - \sigma k\left(\frac{1}{c_0} - \frac{\iota k}{2\pi}\right)\sin k\mathrm{L}} \cos k(x-\mathrm{L}) \,.\, \epsilon^{\iota kat}. \quad (2.92)$$

To find the length of the pipe which will show the strongest resonance to a tone of given frequency, Helmholtz put $\tan k\alpha = \sigma k/c_0$, so that

$$\Omega_{12} = \frac{2\mathrm{F}}{\frac{\cos k(\mathrm{L}+\alpha)}{\cos k\alpha} + \iota\frac{\sigma k^2}{2\pi}\sin k\mathrm{L}} \cos k(x-\mathrm{L}) \,.\, \epsilon^{\iota kat}. \quad (2.93)$$

The pressure and velocity variations in the pipe are thus proportional to

$$2\mathrm{F}\left\{\frac{\cos^2 k(\mathrm{L}+\alpha)}{\cos^2 k\alpha} + \frac{\sigma^2 k^4}{4\pi^2}\sin^2 k\mathrm{L}\right\}^{-\frac{1}{2}}. \quad . \quad (2.94)$$

Helmholtz points out that resonance is greatest when $\cos k(\mathrm{L}+\alpha) = 0$, that is when $(\mathrm{L}+\alpha)$ is equal to an odd number of quarter wave-lengths. α is thus the end-correction to the pipe and can either be calculated or determined experimentally. For pipes with diameters small compared with the wave-lengths we may take $\tan k\alpha = k\alpha$, provided there is no restriction of the orifice, and in this case $\alpha = (\sigma/c_0)$ and therefore $c_0 = (\sigma/\alpha)$. If the cross-section of the pipe is circular and of radius R, $\sigma = \pi\mathrm{R}^2$ and $\alpha = 0{\cdot}82\,\mathrm{R}$, so that $c_0 = (\sigma/\alpha) = 3{\cdot}8\,\mathrm{R}$*.

For a flanged pipe, therefore, (2.91) becomes

$$\beta = -\frac{1 - \frac{1}{2}(k\mathrm{R}^2)^2 - \iota \times 0{\cdot}82\,k\mathrm{R}}{1 + \frac{1}{2}(k\mathrm{R}^2)^2 + \iota \times 0{\cdot}82\,k\mathrm{R}}. \quad . \quad . \quad (2.95)$$

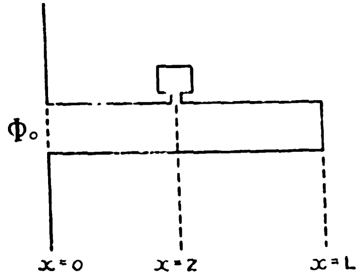
---

* Another method by which c_0 could be found indirectly from experiment is as follows. Place a source of sound inside the pipe near the closed end. If the motions inside the pipe between the open end and the source are examined (say by means of a Rayleigh disk) there will be found a series of positions of maximum and minimum displacement. These may be regarded as being due to interference between the primary wave from the source and the reflected wave from the open end, and as shown above the ratio of the amplitude of the reflected wave to that of the primary is mod β. The value of mod β is easily calculated from the observed ratio of maximum to minimum displacement, and the value of c_0 could then be discovered which gives the best agreement between the value of mod β found in this way and that calculated from (3.41).

§ 3. *Theory of the Boys Double Resonator.*

In the Boys resonator (fig. 2) let the Helmholtz component be attached to the pipe at a distance l from the open end. In that part of the pipe between $x=0$ and $x=l$ there will

Fig. 2.



be a potential, Ω_{12}, of the form given in (2.3). For brevity, let $A_{12}=F+A$, and $A_{21}=F+\beta A$, so that

$$\Omega_{12} = \{A_{12}\epsilon^{ikx}+A_{21}\epsilon^{-ikx}\}\epsilon^{ikat}. \quad . \quad . \quad . \quad (3.1)$$

Let Ω_3 be the potential from $x=l$ to the closed end at $x=L$. Ω_3 will be the potential of stationary waves with a node at $x=L$ and will have the form :

$$\Omega_3 = B\cos k(x-L)\epsilon^{ikat}. \quad . \quad . \quad . \quad . \quad (3.2)$$

Also, since the pressures must be continuous at $x=l$ a necessary condition is $\Omega_{12}=\Omega_3$ when $x=l$, and hence

$$B = \{A_{12}\epsilon^{ikl}+A_{21}\epsilon^{-ikl}\}\operatorname{cosec} k(l-L). \quad . \quad (3.3)$$

Again, if it be assumed that the disturbance due to the Helmholtz resonator causes the motion in the pipe to depart from the plane form indicated in (3.1) and (3.2) only within a region the dimensions of which are small compared with the wave-length, then the current into the Helmholtz resonator can be equated to the difference between the currents across two equipotential surfaces, normal to the axis of the pipe, one on the positive, and the other on the negative side of $x=l$. This condition can be expressed by

$$\sigma\left\{\frac{\partial\Omega_3}{\partial x}-\frac{\partial\Omega_{12}}{\partial x}\right\}_{x=l}=\frac{dq}{dt},$$

$\frac{dq}{dt}$ being the current (c.c. per sec.) into the Helmholtz resonator.

From (3.2) and (3.3) we have

$$\left(\frac{\partial\Omega_3}{\partial x}\right)_{x=l} = -k\{A_{12}\epsilon^{\iota kl} + A_{21}\epsilon^{-\iota kl}\}\tan k(l-\mathrm{L})\,\epsilon^{\iota kat}. \quad (3.51)$$

and from (3.1)

$$\left(\frac{\partial\Omega_{12}}{\partial x}\right)_{x=l} = \iota k\{A_{12}\epsilon^{\iota kl} - A_{21}\epsilon^{-\iota kl}\}\,\epsilon^{\iota kat}. \quad . \quad (3.52)$$

Let $q=q_0\epsilon^{\iota kat}$, so that $\frac{dq}{dt}=\iota kaq_0\epsilon^{\iota kat}$, then substituting from (3.51) and (3.52) in (3.4) we have

$$\begin{aligned}\sigma\,[-k\{A_{12}\epsilon^{\iota kl} + A_{21}\epsilon^{-\iota kl}\}\tan k(l-\mathrm{L})&\\ -\iota k\{A_{12}\epsilon^{\iota kl} - A_{21}\epsilon^{-\iota kl}\}] &= \iota kaq_0, \quad (3.6)\end{aligned}$$

so that

$$\begin{aligned}q_0 &= \frac{\sigma}{a}\,[\iota\{A_{12}\epsilon^{\iota kl} + A_{21}\epsilon^{-\iota kl}\}\tan k(l-\mathrm{L})\\ &\qquad -\{A_{12}\epsilon^{\iota kl} - A_{21}\epsilon^{-\iota kl}\}]\\ &= -\frac{\sigma}{a}\operatorname{cosec} k(l-\mathrm{L})\,[A_{12}\epsilon^{\iota kl} - A_{21}\epsilon^{-\iota kl}]. \quad . \quad . \quad (3.61)\end{aligned}$$

A second expression for q_0 can be obtained by considering the equation of motion of the air in the neck of the Helmholtz resonator. Since the pressure variation is $\rho\frac{d}{dt}(\Omega_{12})_{x=l}$, ρ being the density of the air, this equation is *

$$\frac{d^2q}{dt^2} + 2h\frac{dq}{dt} + \omega_0{}^2 q = c\frac{d}{dt}(\Omega_{12})_{x=l}, \quad . \quad . \quad (3.7)$$

where h is the damping factor of the Helmholtz resonator, c is the hydrodynamical conductance of the neck, and $\omega_0{}^2=a^2c/\mathrm{Q}$, Q being the internal volume of the resonator and a the velocity of sound. ω_0 is equal to 2π times the resonance frequency of the Helmholtz component. Thus, writing ω for ka, we have

$$q_0 = \frac{\iota\omega c}{(\omega_0{}^2-\omega^2)+2\iota\omega h}\{A_{12}\epsilon^{\iota kl} + A_{21}\epsilon^{-\iota kl}\}. \quad . \quad (3.71)$$

Or, if Δ is written for $\omega_0(\omega_0/\omega - \omega/\omega_0)$,

$$q_0 = \frac{c}{2h-\iota\Delta}\{A_{12}\epsilon^{\iota kl} + A_{21}e^{-\iota kl}\}. \quad . \quad . \quad (3.72)$$

---

* Rayleigh, 'Theory of Sound,' vol. ii. p. 198.

Equating the values of q_0 in (3.61) and (3.72), we obtain

$$A_{12}\epsilon^{\iota kL}-A_{21}\epsilon^{-\iota kL}$$

$$=-\frac{ac}{\sigma(2h-\iota\Delta)}\cos k(l-L)\,\{A_{12}\epsilon^{\iota kl}+A_{21}\epsilon^{-\iota kl}\}, \qquad (3.8)$$

so that

$$A_{21}=A_{1}{}^{2}\,\frac{\epsilon^{\iota kL}+\dfrac{ac}{\sigma(2h-\iota\Delta)}\cos k(l-L)\,.\,\epsilon^{\iota kl}}{\epsilon^{-\iota kL}-\dfrac{ac}{\sigma(2h-\iota\Delta)}\cos h(l-L)\,.\,\epsilon^{-\iota kl}}$$

$$=A_{12}\epsilon^{2\iota kL}\,\frac{1+\dfrac{ac}{\sigma(2h-\iota\Delta)}\cos k(l-L)\,.\,\epsilon^{\iota k(l-L)}}{1-\dfrac{ac}{\sigma(2h-\iota\Delta)}\cos k(l-L)\,.\,\epsilon^{-\iota k(l-L)}}. \qquad (3.81)$$

Let

$$\mu=(A_{21}/A_{12})\epsilon^{-2\iota kL}. \quad . \quad . \quad . \quad . \qquad (3.82)$$

Then

$$\frac{A_{21}}{A_{12}}=\mu\epsilon^{2\iota kL}=\frac{F+\beta A}{F+A}. \quad . \quad . \quad . \qquad (3.83)$$

Hence

$$A=-\frac{1-\mu\epsilon^{2\iota kL}}{\beta-\mu\epsilon^{2\iota kL}}F. \quad . \quad . \quad . \quad . \qquad (3.84)$$

Thus

$$q_0=\frac{cA_{12}}{2h-\iota\Delta}(\epsilon^{\iota kl}+\mu\epsilon^{2\iota kL}\epsilon^{-\iota kl})$$

$$=\frac{c}{2h-\iota\Delta}\,\frac{(\beta-1)F}{\beta-\mu\epsilon^{2\iota kL}}(\epsilon^{\iota kl}+\mu\epsilon^{2\iota kL}\epsilon^{-\iota kl})$$

$$=\frac{c}{2h-\iota\Delta}\,\frac{(\beta-1)F}{\beta\epsilon^{-\iota kL}-\mu\epsilon^{\iota kL}}\{\epsilon^{\iota k(l-L)}+\mu\epsilon^{-\iota k(l-L)}\}. \qquad (3.9)$$

The theory of the Helmholtz resonator shows that the value of q_0 corresponding to a primary potential $\phi_0\epsilon^{\iota kat}$ at the mouth of the resonator is

$$q_0=\frac{c}{2h-\iota\Delta}\phi_0\,; \quad . \quad . \quad . \quad . \qquad (3.91)$$

so that (3.9) indicates that, in the case of the Boys resonator, the current in the neck of the Helmholtz component is the same as would be induced, in an unenclosed space, by a primary potential

$$\cdot\ \frac{(\beta-1)F}{\beta\epsilon^{-\iota kl}-\mu\epsilon^{\iota kL}}\{\epsilon^{\iota k(l-L)}+\mu\epsilon^{-\iota k(l-L)} \quad . \quad . \quad . \qquad (3.92)$$

The theory of the simple stopped-pipe resonator, as given in § 2, shows that the potential at a distance from the open end is (*cf.* equation (2.5)):

$$\frac{(\beta-1)\mathrm{F}}{\beta\epsilon^{-\iota k\mathrm{L}}-\epsilon^{\iota k\mathrm{L}}}\{\epsilon^{\iota k(l-\mathrm{L})}+\epsilon^{-\iota k(l-\mathrm{L})}\}. \quad . \quad . \quad (3.93)$$

Hence, comparing (3.92) and (3.93), we see that the factor μ occurring in both numerator and denominator of (3.92) represents the reaction of the Helmholtz resonator on the potential within the pipe. As would be expected, the reaction depends not only on the distance of the resonator from the closed end but also upon its damping, tuning, the conductance of the orifice, and the cross-sectional area of the pipe.

Equation (3.9) completes the solution of the problem so far as it is required for present purposes, for it enables us to calculate the amplitude of the air displacements in the neck of the Helmholtz resonator for any combination of pipe and resonator within the limits imposed by the assumption as to the smallness of the diameter of the pipe relative to the wave-length.

For the purpose of numerical calculation it is convenient to make use of the conception of what may be called the "magnification" of the resonator.

As stated previously, the function of the double resonator is to magnify the vibrations occurring in the incident sound-wave so that they may be easily recorded by the detector, the latter being placed in the narrow neck of the Helmholtz component. A proper measure of the magnification due to the resonator is therefore the ratio of the maximum velocity (or displacement) occurring in the neck of the Helmholtz resonator to the maximum velocity (or displacement) occurring in the incident sound-wave *.

If A is the cross-sectional area of the neck of the Helmholtz component, the maximum velocity occurring in the neck is $\frac{1}{\mathrm{A}}\left|\frac{dq}{dt}\right|$. The maximum velocity in the incident plane wave $\mathrm{F}\epsilon^{\iota k(at-x)}$ is $|\iota k\mathrm{F}|$, but owing to reflexion the pressure variation due to the incident wave at the mouth of the resonator is double what it would be if there were no flange. The question arises as to whether the (supposed infinite) flange is or is not to be regarded as part of the resonator. The best way out of this difficulty is probably to adopt as the standard of comparison that velocity which in a plain progressive wave would be associated with a pressure-variation equal to that due to the primary wave at the mouth of the resonator—in this case $|2\iota k\mathrm{F}|$. Thus, if M denote the magnification :

---

* *Cf.* 'Science Progress,' vol. xx. p. 69 (1925).

$$\mathrm{M} = \left(\frac{1}{\mathrm{A}}\left|\frac{dq}{dt}\right|\right)\Big/|2\iota k\mathrm{F}|. \quad . \quad . \quad . \quad (3.94)$$

Whence, from (3.9),

$$\mathrm{M} = \frac{1}{2}\frac{a}{\mathrm{A}}\left|\frac{c}{2h-\iota\Delta}\,\frac{\beta-1}{\beta\epsilon^{-\iota k\mathrm{L}}-\mu\,\epsilon^{\iota k\mathrm{L}}}\left\{\epsilon^{\iota k(l-\mathrm{L})}+\mu\,\epsilon^{-\iota k(l-\mathrm{L})}\right\}\right|. \quad (3.95)$$

Some numerical values of M, showing the variation with frequency of the incident sound, are given in the next section.

§ 4. *Numerical Results.*

In this section a short account is given of the calculation of M by means of (3.95) in the case of a Boys resonator in which both components (Helmholtz resonator and stopped pipe) have a fundamental frequency (n_0) of 256 vibrn./sec.

The dimensions and other characteristics of the Helmholtz resonator were taken to be such as are normally employed for the construction of hot-wire microphones, the actual values selected being the following :—

Diameter of orifice $= d = 0{\cdot}5$ cm.
Conductance of orifice $= c = 0{\cdot}125$ cm.
Damping factor at 256 vibrn./sec. $= h = 50$ sec.$^{-1}$.

The magnification associated with the Helmholtz resonator when used alone appears as a factor in the expression for M given in (3.95), for it is easily shown that it is equal to

$$\frac{a}{\mathrm{A}}\left|\frac{c}{2h-c\Delta}\right|.$$

So that, if this is denoted by M_1, (3.95) can be written :

$$\mathrm{M} = \mathrm{M}_1 \times \frac{1}{2}\left|\frac{\beta-1}{\beta\epsilon^{-\iota k\mathrm{L}}-\mu\,\epsilon^{\iota k\mathrm{L}}}\left\{\epsilon^{\iota k(l-\mathrm{L})}+\mu\,\epsilon^{-\iota k(l-\mathrm{L})}\right\}\right|. \quad (4.1)$$

Values of M_1 corresponding to values of the interval n/n_0 between 0·80 and 1·20 are given in Table I. The velocity of sound (a) has been taken to be 33760 cm./sec.

In calculating M_1 it has been assumed that the damping factor h remains constant throughout the range of frequencies dealt with. In practice it is found that h varies with frequency, but the information at present available is insufficient to allow this fact to be taken into consideration.

The magnification associated with the stopped pipe is seen from (2.5) to be

$$M_2 = \left| \frac{\beta - 1}{\beta \epsilon^{-ikL} - \mu \epsilon^{ikL}} \right| . \quad . \quad . \quad . \quad . \quad (4.2)$$

M_2 can also be introduced as a factor in the expression for M, but for numerical calculation it is generally better to retain M in the form given in (4.1). It is of interest, however, to compare the magnification belonging to the pipe-component with that obtainable from the double resonator, and for this reason some values of M_2 have been included in Table I.

The reduced length of the pipe is equal to a quarter of the fundamental wave-length, that is, to $a/4n_0$. Hence, if R is the radius of the cross-section,

$$L + 0{\cdot}82\,R = a/4n_0 . \quad . \quad . \quad . \quad . \quad (4.3)$$

In order to define the shape of the pipe (that is, the ratio of length to diameter), let $L = mR$. We then have from (4.3)

$$\left.\begin{aligned} R &= \frac{a}{4n_0} \frac{1}{m + 0{\cdot}82} \\ L &= \frac{a}{4n_0} \frac{m}{m + 0{\cdot}82} \end{aligned}\right\} . \quad . \quad . \quad . \quad . \quad (4.4)$$

Hence

$$kR = \frac{\pi}{2} \frac{n}{n_0} \frac{1}{m + 0{\cdot}82}, \quad . \quad . \quad . \quad . \quad (4.51)$$

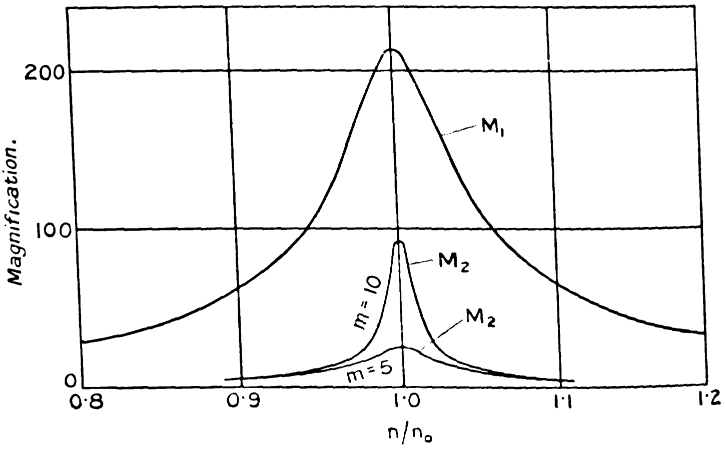
$$kL = \frac{\pi}{2} \frac{n}{n_0} \frac{m}{m + 0{\cdot}82} . \quad . \quad . \quad . \quad . \quad (4.52)$$

To show the effect of changing the cross-sectional area of the pipe, the two cases $m = 5$ and $m = 10$ were selected for calculation. Values of β were first calculated by means of (2.95) from the values of kR given by (4.51). Corresponding values of kL were then found from (4.52) and finally M_2 computed by means of (4.2). The values of M_2 so found are given in Table I.

TABLE I.

n/n_0.	M_1.	M_2.		n/n_0.	M_1.	M_2.	
		$m=5$.	$m=10$.			$m=5$.	$m=10$.
0·80	29	—	—	1·02	181	21	—
2	33	—	—	4	133	14	—
4	38	—	—	6	101	10	11
6	43	—	—	8	80	8	8
8	51	—	—	10	67	6	6
90	61	6	6	2	57	—	—
2	75	7	8	4	49	—	—
4	96	10	10	6	44	—	—
6	130	13	—	8	39	—	—
8	180	20	30	1·20	36	—	—
1·00	215	28	95				

Fig. 3.



In fig. 3, M_1 and M_2 are plotted against n/n_0. It will be seen that the magnification due to the Helmholtz resonator is much greater than that obtainable from the stopped pipe. The increased sharpness of resonance shown by M_2 when m is changed from 5 to 10 is very marked, the reason being that sound-energy escapes less readily from the narrower pipe.

The calculation of M for the double resonator by means of (4.1) presents no difficulty. A preliminary calculation of μ is necessary, and this can be effected by means of the formula

$$\mu = \frac{1 + \dfrac{ac}{\sigma(2h - \iota\Delta)} \cos k(l - \mathrm{L}) \,.\, \epsilon^{\iota k(l-\mathrm{L})}}{1 - \dfrac{ac}{\sigma(2h - \iota\Delta)} \cos k(l - \mathrm{L}) \,.\, \epsilon^{-\iota k(l-\mathrm{L})}} . \quad . \quad (4.6)$$

σ is the cross-sectional area of the pipe, so that

$$\sigma = \pi \mathrm{R}^2 = \pi \left(\frac{a}{4n_0} \frac{1}{m + 0{\cdot}82} \right)^2 . \quad . \quad . \quad (4.7)$$

The following three cases were selected for the calculation of M :—

Case I. $m=5$, $l=\mathrm{L}$.—The Helmholtz resonator is here at the closed end of the pipe.

Case II. $m=10$, $l=\mathrm{L}$.—The Helmholtz resonator is again at the closed end of the pipe, but the diameter of the latter is only about half its vale in Case I.

Case III. $m=10$, $l=0{\cdot}3\,\mathrm{L}$.—The diameter of the pipe is the same as in Case II, but the Helmholtz resonator is inserted through the wall of the pipe at a distance of $0{\cdot}3\,\mathrm{L}$ from the open end.

The numerical values of M calculated for these three cases are given in Table II.

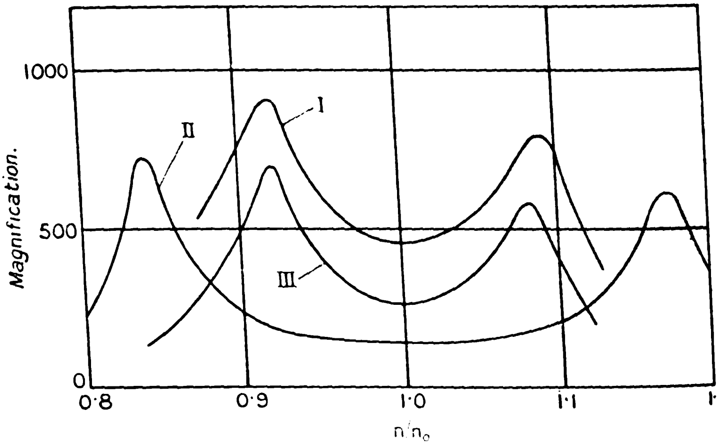
Table II.

n/n_0.	I. $m=5$.	II. $m=10$.	III. $m=10$.
0·80	—	230	—
2	—	416	—
4	—	733	137
6	—	487	210
8	598	309	326
90	770	231	504
2	910	191	698
4	699	169	461
6	554	—	—
8	485	149	292
1·00	463	146	274
1·02	476	—	281
4	534	—	—
6	635	171	426
8	773	186	587
1·10	743	217	436
2	450	270	229
4	—	369	—
6	—	545	—
8	—	578	—
1·20	—	344	—

These values of M are plotted against n/n_0 in fig. 4, in which the vertical scale is only one-fifth of that used in fig. 3. The following points may be noted in connexion with these curves:—

(i.) The curve I ($m=5$, $l=L$) shows the greatly increased magnification obtained by the use of double resonance. It will be seen from Table I, or fig. 3, that the greatest magnifications obtainable from the Helmholtz resonator or stopped pipe alone are 215 and 28 respectively. When the two are combined, however, the magnification does not fall below 450 between $n/n_0=0{\cdot}86$ to $n/n_0=1{\cdot}12$, that is from 220 to 287 vibrn./sec.; while at $n/n_0=0{\cdot}92$ and $n/n_0=1{\cdot}085$ it rises to 910 and 810 respectively.

Fig. 4.



(ii.) The curve II ($m=10$, $l=L$) shows the effect of reducing the cross-sectional area of the pipe. Although the magnification obtainable from the pipe alone is greater than in Case I, namely, 95 as compared with 28, the reduction in cross-section has been accompanied by a tightening of the coupling between the two components, with the result that the two resonance frequencies of the double resonator are further apart, and the general level of the magnification is lowered. The small variation in magnification in the region between about $n/n_0=0{\cdot}96$ and $1{\cdot}04$ is noticeable. Instruments made with double resonators of this type are useful in cases in which it is required to record the strength of a sound the pitch of which is liable to undergo small variations.

(iii.) The resonance frequencies as found from the curve in fig. 4 show a satisfactory agreement with those calculated from the simple formula previously obtained by neglecting the loss of sound-energy from the resonator. Thus, curve I shows that resonance frequencies occur at approximately $n/n_0=0{\cdot}92$ and $1{\cdot}09$, while the formula previously given *, which may be written

$$\tan\frac{\pi}{2}\frac{n}{n_0}=\frac{\sigma}{ac}\Delta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.8)$$

indicates that resonance frequencies occur when $n/n_0=0{\cdot}91$ and $1{\cdot}09$. Similarly, curve II indicates resonance at $n/n_0=0{\cdot}84$ and $1{\cdot}17$, these values being identical with those found from a graphical solution of (4·8).

(iv.) The curve III shows the effect of moving the Helmholtz resonator towards the open end of the pipe. The resonance peaks are brought nearer together again, and occupy nearly the same positions as when $m=5$. The general level of the magnification is raised, but is maintained for a smaller range of frequencies. Previous experiments have indicated that enhanced sensitiveness may sometimes be obtained by a suitable choice of the distance of the Helmholtz resonator from the open end of the pipe. The conditions under which this may occur should be derivable from the equations contained in the present paper, but a full investigation has not yet been carried out.

§ 5. *Experimental Results.*

Some observations will now be described which were undertaken with the object of providing an experimental check on the theory developed in the preceding sections.

No means being available for measuring the actual value of the magnification of resonators, attention was directed to obtaining resonance curves the forms of which could be compared with the theoretical curves shown in fig. 4. For this purpose a singly resonated hot-wire microphone was chosen with a natural frequency of 256 vibrn./sec. The characteristics of the Helmholtz resonator were very nearly the same as those used in § 4, their actual values being $c=0{\cdot}115$ cm., $h=49$ sec.$^{-1}$.

For combining with this Helmholtz resonator, two ebonite stopped-pipes were made whose dimensions were (*a*) $L=29$ cm., $2R=12{\cdot}1$ cm; (*b*) $L=31$ cm., $2R=5{\cdot}7$ cm. Thus for the pipe (*a*) we have $m=4\cdot8$, and for the pipe (*b*), $m=10\cdot9$.

---

* Equation (12), Proc. Roy. Soc. A, ci. p. 395 (1922).

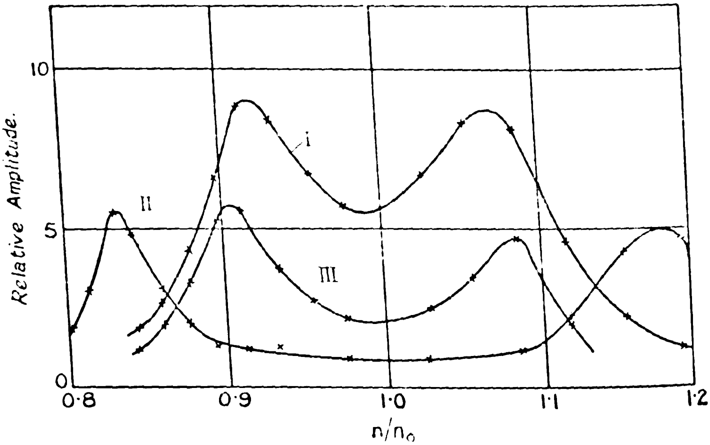
To correspond with the three cases dealt with in § 4, the following arrangements of Helmholtz resonator and pipe were made :—

I. The orifice of the Helmholtz resonator was inserted through the closed end of the wider pipe. Thus $m=4\cdot8$, $l=\mathrm{L}$.

II. The orifice of the Helmholtz resonator was inserted through the closed end of the narrower pipe, so that $m=10\cdot9$, $l=\mathrm{L}$.

III. The orifice of the Helmholtz resonator was inserted through the wall of the narrower pipe at a distance $\frac{3}{10}$ L from the open end so that $m=10\cdot9$, $l=\frac{3}{10}\mathrm{L}$.

Fig. 5.



The experimental resonance curves for these three cases are shown in fig. 5, the crosses indicating the observed points. The method by which they were obtained was substantially that described in previous papers. The source of sound was provided by a specially designed thermionic valve oscillator, the current from which actuated the diaphragm of a "loud-speaker." To avoid inequalities in acoustic output due to resonances, the horn of the loud-speaker was removed.

The observations were made in the open, the resonators to be examined being laid on the ground at a distance of 0·8 metre from the source of sound. The surface of the ground thus represented the infinite flange assumed in the theory.

The bridge method of observing the response of the hot-wire grid was employed, the ohmic changes being proportional to the square root of the deflexions shown on a microammeter. The scale of relative amplitudes employed in fig. 5 was thus arrived at by taking the square root of the observed deflexions. The hot-wire grids employed were of standard type with hot resistance about 330 ohms and maximum safe working current of 27 milliamperes. A relative amplitude of 10 in fig. 5 corresponds to a resistance change of about 1 ohm.

A comparison of fig. 5 with fig. 4 shows that, having regard to the small disparities between the dimensions and other characteristics of the resonators used in practice with those assumed in the theory, the agreement between the observed and calculated curves is satisfactory and indicates that the theory as developed in § 4 is substantially correct.

Improvement could probably be effected by obtaining a more accurate value for β and by taking into account the variation of h with frequency.

§ 6. *Summary.*

A theory of the "Boys" type of double resonator is developed in which allowance is made for the loss of sound-energy from the resonator owing to (i.) the dissipation of sound into heat by the operation of viscous forces in the narrow neck leading into the Helmholtz resonator, and (ii.) the escape of sound into the surrounding air through the open end of the pipe component. Some numerical results are given which show the changes indicated by theory in the form of the resonance curves caused by (*a*) diminishing the cross-sectional area of the pipe, and (*b*) moving the Helmholtz resonator from the closed end towards the open end of the pipe. The forms of the calculated resonance curves are found to be in fair agreement with observations. The resonance frequencies as found from the more complete theory now given agree well with those found from the approximate theory previously developed.

Air Defence Experimental Establishment,
Woolwich.
May, 1926.

LXVIII. *Regularities in the Spectrum of Ionized Silver.*
By C. S. BEALS, *M.A.*, *D.I.C.*[*]

[Plate XIV.]

INTRODUCTORY.

THE arc spectra of copper, silver, and gold, elements occupying the sub-group in the first column of the periodic table, have been shown to be similar in that they all three contain doublet series. According to the view recently advanced by Sommerfeld, however, the arc spectrum of silver would be expected to be of a more simple character than the corresponding spectra of copper and gold. It was formerly believed that the character of the terms in a spectrum was entirely determined by the azimuthal quantum numbers associated with successive orbits occupied by the outermost electron of the atom. According to more recent theories of atomic structure as advanced by Russell and Saunders [†], Heisenberg [‡], Hund [§], and others, the character of a spectral term is determined by what may be called a group quantum number which depends on the resultant of the moments of momenta of all the electrons external to the rare-gas-like core of the atom. The simple character of the spectra of the alkali metals has accordingly been attributed to the fact that they each have but a single electron external to the rare-gas-like core. The prediction which was made by Sommerfeld that the spectrum of silver would be similar to those of the alkali metals in containing only doublet terms, is based on the belief that the atomic configuration which obtains for palladium (the element preceding silver in the periodic table) partakes somewhat of the rare-gas-like character. The atomic structure of palladium consists of a completed shell of 10 4_3 electrons external to the rare-gas-like (Krypton) core. This configuration of electrons apparently possesses an inherent stability somewhat similar to that which obtains for the atoms of the rare-gases. As a consequence of this, when a single electron is added to form the silver atom the nature of the terms in the spectrum should depend solely on the successive orbits occupied by this single outer electron. The spectrum would thus be expected to be alkali-like in character, and to contain only doublet terms.

---

[*] Communicated by Prof. A. Fowler, F.R.S.

[†] Russell & Saunders, Astrophys. Journ. vol. lxi. p. 38 (1925).

[‡] Heisenberg, *Zeit. f. Phys.* vol. xxxii. p. 841 (1925).

[§] Hund, *Zeit. f. Phys.* vol. xxxiii. p. 335 (1925).

The spectrum of copper is less simply related to those of the alkalies. The arrangement of doublet series terms in the spectrum of copper would appear to indicate that the atom of copper in its normal state is exactly analogous with that of silver and consists of a shell of 10 3_3 electrons and a single 4_1 electron external to the rare-gas-like (argon) core. The distinction between the two is believed to be found in the smaller stability of the shell of 10 3_3 electrons in the atom of copper. This is evidenced by the fact (believed to be established by spectroscopic data) that of the 10 electrons external to the argon core in the neutral atom of nickel, only 8 occupy 3_3 orbits, the remaining two being found in 4_1 orbits, From this it may be inferred that terms in the spectrum of copper may not only be due to successive orbits occupied by the valence electron, but may also be affected by the displacement of additional electrons from 3_3 orbits to outer orbits when the atom is in an excited condition. These considerations have led Hund * to predict the appearance of quartet terms in the spectrum of copper. As the atomic configuration for gold is believed to be closely analogous with that of copper, it seems reasonable to extend Hund's prediction to include the spectrum of gold.

In so far as experimental data are at present available, they are in agreement with the theoretical predictions contained in the preceding paragraph. The spectrum of copper † has already been shown to contain quartet terms in addition to its doublet series system, while evidence is not lacking that a quartet system will presently be shown to be a feature of the gold spectrum ‡.

The arc spectrum of silver contains a smaller number of lines than the corresponding spectra of copper and gold, and a majority of these lines have been shown to belong to a doublet system. The unclassified lines, which are found mainly in the ultra-violet, form a very puzzling feature of the silver arc spectrum. There is no evidence at present available which would connect them with a quartet system, while at the same time it seems fairly certain that they do not form part of the regular doublet

---

* Hund, *Zeit. f. Phys.* vol. xxxiii. p. 335 (1925).

† Beals, Proc. Roy. Soc. A, vol. cxi. (May 1926).

‡ McLennan & McLay, Proc. Roy. Soc. A, vol. cviii. p. 515 (1925).

series. Many of these lines show curious fluctuations in intensity. For example, the lines λ 2309·63 and λ 2374·90 are very diffuse and so strong as to dominate the spectrum in this region under ordinary arc conditions. When the arc is passed *in vacuo* they disappear completely. It seems possible that some of these lines may form an anomalous feature of the silver spectrum, which has no counterpart among previously recognized spectral structures.

From what has already been said concerning the structure of the silver atom, it may be deduced that the removal of the outer 5_1 electron would leave a configuration closely resembling that found in the atom of neutral palladium; *i.e.*, a completed shell of 10 4_3 electrons external to the rare-gas-like core of the atom. The spectrum of the singly-ionized atom of silver would accordingly be expected to resemble in its general features the arc spectrum of palladium. Fortunately, the necessary data concerning the palladium spectrum are now available, analyses of this spectrum having been published by the present writer *, by Catalan †, and by McLennan and Smith ‡. Most of the strong palladium arc lines have been included in a singlet and triplet system. The frequencies of these lines have been shown to be due to transitions from a number of levels defined by the terms ^3P, $^3D'$, ^3F, ^1P, $^1D'$, ^1F to a number of lower levels corresponding to the terms ^1S, ^3D, and ^1D. The ^1S term has been found to be the fundamental term, a fact that had been predicted on theoretical grounds by Hund and Catalan. Since the atomic confiurations for Pd I and Ag II are believed to be precisely analogous, a ^1S term should also appear as the fundamental term of the Ag II spectrum. The other terms of the palladium spectrum would also be expected, but it is not certain that they would appear in the same order.

The present paper contains the results of an investigation of the first spark spectrum of silver. The work has included the separation of Ag II lines from arc lines and lines corresponding to higher ionizations, a study of Zeeman effects, and a discussion of the numerical relations which have been found to exist in the Ag II spectrum.

---

* Beals, Proc. Roy. Soc. A, vol. cix. p. 369 (1925).

† Catalan, *Zeit. f. Phys.* vol. xxxv. p. 449 (1926).

‡ McLennan & Smith, Trans. Roy. Soc. Canada, vol. xx. p. 1 (Jan. 1926).

THE SEPARATION OF ARC AND SPARK LINES.

In order to sort out the enhanced lines and to assign them to a particular stage of ionization, the spectrum of silver was observed under varying intensities of excitation. The most useful sources of light for this purpose were an ordinary arc in air and a strongly-condensed spark obtained with a large resonance transformer. Intermediate stages between the arc and spark could be obtained by employing varying amounts of inductance in the spark circuit. Some difficulty was experienced due to the masking of lines by band spectra, and this was remedied by passing the arc and spark in hydrogen.

The behaviour of arc and spark lines is illustrated in Pl. XIV., in which arc and spark photographs have been compared. The lines corresponding to the first ionization (Ag II) are fairly strong in the arc and might easily be mistaken for arc lines. In the spark spectrum the Ag II lines are strongly enhanced, while the arc lines become weaker. The spark photographs which were obtained without the use of inductance in the spark circuit show a large number of lines which do not appear or are extremely feeble in the arc. It appears probable that these lines may belong to the second or higher ionization.

Those lines which are considered to belong to the spectrum of singly ionized silver have been included in Table I. In this table is indicated the wave-length and wave-number of each line and an estimate of its relative intensity. Wherever possible Eder's wave-lengths have been used, and where they are not available the values of Exner and Haschek and Huppers have been given. The region of the spectrum which has been examined extends from λ 6500–1850, but no lines of wave-length longer than λ 3000 have definitely been assigned to the spectrum of Ag II.

OBSERVATIONS OF ZEEMAN EFFECTS.

Unfortunately, many of the shorter wave-length lines of Ag II lie in a region of the spectrum which is not accessible to ordinary Zeeman Effect observations. It has not been found possible to use the higher orders of the grating for observation of lines below λ 2240, and the wave-length separation of components in this region of the spectrum is so small that first- and second-order observations are of little use. As a consequence of this the Zeeman measurements are limited to those lines which occur in the region λ 2240–2940.

TABLE I.

λ.	(Int.).	ν.	Zeeman Effect.	Combination.
2929·37	(3)	34127·1	0·90	D–L
2767·54	(4)	36122·5	(0·00)0·97	D–N
2660·49	(3)	37575·9	......	D–O
2535·30	(4)	39431·3	0·81	C–L
2506·63	(4)	39882·3	0·84	C–M
2473·84	(4)	40410·7	(0·00)1·53	D–P
2447·93	(5)	40838·5	(0·28)1·00	
2437·81	(10)	41008·0	(0·00)1·18	B–L
2413·21	(9)	41426·1	(0·00)1·04	C–N
2411·37	(5)	41457·6	(0·00)1·23	B–M
2357·92	(4)	42397·3	(0·00)0·44	
2331·36	(5)	42880·2	(0·00)0·99	C–O
2324·65	(6)	43002·9	0·76	B–N
2320·23	(5)	43086·0	(0·00)1·18	D–Q
2317·03	(5)	43145·5	(0·00)1·30	
2279·96	(5)	43846·8	(0·00)1·04	D–R
2248·72	(4)	44455·9	0·83	B–O
2246·37	(6)	44502·4	(0·00)1·19	
2229·49	(6)	44839·4		
2186·73	(6)	45716·0	......	C–P
2166·42	(6)	46144·6	......	A–L
2145·55	(7)	46593·3	......	A–M
2120·36	(6)	47146·9		
2113·76	(7)	47294·1	......	B–P
2065·82	(8)	48390·8	......	C–Q
2033·84	(3)	49152·1	......	C–R
2015·72	(5)	49594·0		
2000·56	(6)	49969·8	......	B–Q
1993·55	(6)	50145·4	......	C–S
1932·76	(4)	51722·3	......	B–S

The experimental arrangements for the observation of Zeeman effects has already been described *, and has been used without sensible alteration in the present work. An arc in air between silver poles served as a source of light. The Ag II lines appear in the spark with considerably greater intensity than in the arc, but they are less clearly defined and a number of them show definite reversals. For

---

* Beals, Proc. Roy. Soc. A, vol. cix. p. 369 (1925).

this reason sole reliance has been placed in the arc, and little difficulty has been experienced in obtaining the lines with sufficient intensity. The photographs have been taken in the third, fourth, and fifth orders of a 10-foot concave grating. Times of exposure have varied from 30 minutes to 2 hours.

The measurements of Zeeman components have been included in Table I. In accordance with the usual practice, the separations have been expressed in terms of the normal Zeeman effect as shown by the separation of components in lines of a singlet system. The value of the normal Zeeman effect has been derived from the two calcium lines λ 3933·66 and λ 3968·46 which appeared as impurities in the silver spectrum. The resolutions shown by these line are as follows :—λ 3933·66, (·33) 1·00, 1·66, λ 3968·46, (·66) 1·33.

Structure of the Spectrum.

As a first step in the analysis of the Ag II spectrum a search was made for any constant wave-number differences which might exist among the lines. A number of such relations have been discovered, and the results of this part of the investigation have been incorporated in Table II. As a consequence of the numerical relations, it is possible to express the wave-numbers of many of the lines as differences between a comparatively small number of terms or energy levels. These terms have also been given in Table II. It is, of course, not possible to assign absolute values to these terms, but the relative values can be given with considerable accuracy. Approximately two-thirds of the lines of Table I. have been included in this term system. The failure to account for the remaining lines has been attributed, in part

Table II.

	A.	B.	C.	D.
	100,000·0	94,863·9	93,287·1	87982·2
		(5136·1)	(1576·8)	(5304·9)
L 53855·5......	46144·6(6)	41008·0(10)	39431·3(4)	34127·1(3)
M 53405·9......	46593·3(7)	41457·6(5)	39882·3(4)	
N 51860·9......	......	43002·8(6)	41426·1(9)	36122·5(4)
O 53407·7......	......	44455·9(4)	42880·2(5)	37575·9(3)
P 47570·8......	......	47294·1(7)	45716·0(6)	40410·7(4)
Q 44895·5......	......	49969·8(6)	48390·8(8)	43086·0(5)
R 44135·0......		......	49152·1(3)	43846·8(5)
S 43141·6......	......	51722·3(4)	50145·4(6)	

at least, to the lack of observational data in the region of the spectrum below λ 1850. The large value of the term separations makes it reasonable to suppose that a number of lines, in the region of the spectrum which has been observed, may be connected by constant difference relations with lines in the Schumann region. For example, wave-numbers calculated from the combinations A–Q, A–R, A–S all fall in the region below λ 1850.

While Zeeman effects have been observed for some of the lines, the resolution obtained is not sufficiently high to enable any of the terms to be identified with certainty. It is possible, however, by a consideration of the general form of some of the patterns, to gain some information as to the relative values of the inner quantum numbers. In their recent work, 'Zeemaneffekt und Multiplettstruktur,' Back and Landé have formulated the following rule, which experiment has shown to be generally valid for a system of odd multiplicities: "For the Zeeman pattern given by the combination of two terms X and Y, the central component has zero intensity when $j_x = j_y$." By the application of this rule to a number of the Zeeman patterns of lines involved in Table II., it may be deduced that the terms C and D have the same inner quantum number. By assigning an arbitrary value to this quantum number, relative quantum numbers may be deduced for a number of the other terms. This method has not so far led to the identification of any complete multiplet groups, but it should prove useful when the required additional wave-length data become available.

Since the terms of the Ag II spectrum have not as yet been definitely identified, it is scarcely possible to make a very useful comparison between this spectrum and that of the neutral atom of palladium. In the present state of our knowledge of the subject, it seems scarcely justifiable to make the assumption that the arrangement of terms in the two spectra will be precisely analogous. If such an assumption were made, however, the following would appear to be the most probable arrangement of the larger terms of Table II. The term D should correspond with the palladium term $^1D_2$. The terms A, B and C would make up a partially-inverted triplet D level in which $A = {}^3D_3$, $B = {}^3D_1$, and $C = {}^3D_2$. The lines formed by combinations with the fundamental ^1S level would probably fall in the Schumann region, and so would not come within the range of the present investigation. Too much importance should not be attached to this suggestion, as the evidence in favour of it is far from complete and the non-appearance of the combinations D–M and D–S is against it.

In considering other points of similarity with the palladium spectrum, it is perhaps worth while to mention that many of the Ag II lines are strongly reversed when observed under spark conditions, and also that they appear with considerable intensity in a flame arc produced *in vacuo*. This indicates that they are "low-level" lines, and as such they correspond with those lines of palladium which have been investigated by the present writer. It may further be noted that the Ag II lines, as compared with those of neutral palladium, show the displacement toward the ultra-violet and the increased value of the term separations which observation of analogous arc and spark spectra of other elements would lead us to expect.

SUMMARY.

New observations of the spectrum of silver have been made with the object of discovering any regularities which may occur among the lines corresponding to a single ionization of the silver atom. The work has included a study of the spectrum under varying intensities of excitation. Zeeman measurements have also been made for a number of the lines.

Thirty lines in the region λ 1850–2930 have definitely been assigned to the spectrum of Ag II. Of these, somewhat over two-thirds have been included in a system of constant wave-number differences involving terms which show some evidence of analogy with the terms found in the arc spectrum of palladium.

The work has served to emphasize the need for an extension of the observations of the silver spectrum to the extreme ultra-violet region of the spectrum. It seems probable that a clear understanding of the Ag II spectrum must await new wave-length data in the Schumann region. Such data should include, not only actual measurements of wave-length, but also a careful comparison of intensities in the arc and spark. It is to be regretted that lack of such observations has made the present investigation incomplete. The results which have been obtained should, however, provide a sound basis for further research, and it is confidently expected that the constant difference relations which have been discovered will provide the key for a complete analysis of the Ag II spectrum.

In concluding the paper the writer wishes to express to Professor Fowler his appreciation of the opportunity of carrying out the experiments, and to thank him also for kind interest and encouragement during the progress of the work.

LXIX. *A Simple Integraph.*

By ALFRED A. ROBB, *Sc.D.*, *F.R.S.*[*]

IF a sharp rounded edge, such as the end of a knife-blade, is pressed against a plane surface of paper it can move freely in a direction tangential to itself, but not freely in a transverse direction.

With suitable guidance such an edge can be made to trace out a curve on the sheet of paper, which can quite clearly be seen as an indentation in the latter. A small sharp-edged wheel turning on an axle may, with advantage, be substituted for the knife-edge.

This principle may be taken advantage of in the construction of an exceedingly simple integraph in the following way.

A small drawing-board is mounted on three supports forming a sort of little table—one of these supports being a rounded knife-edge or a small sharp-edged wheel, as above described, and the others being smooth rounded studs which can move freely in any direction over a flat surface of paper.

For convenience I shall refer to this part of the apparatus as the "*table*," to distinguish it from a larger drawing-board upon which the "table" is placed, and which I shall refer to briefly as the "*drawing-board*." This latter is simply an ordinary drawing-board of suitable size.

To the drawing-board is clamped an arrangement bearing a tracing point of some sort, which remains fixed with respect to the drawing-board, so that the "table," while sliding over the drawing-board, can move freely underneath the tracing point.

Let us suppose now that a curve is drawn on a piece of paper and that the latter is fixed by means of drawing-pins to the "table."

Let us further suppose that a plane sheet of paper is fixed on the surface of the drawing-board and the "table" placed on the top of it.

A suitable weight is put on the "table" so that the wheel may make a visible indentation on the paper below it when the "table" is caused to slide over the latter.

The "table" is now guided so that the tracing point traverses the curve. When this is done the wheel will trace out a second curve, and the relation between the two curves is very simple.

---

[*] Communicated by the Author.

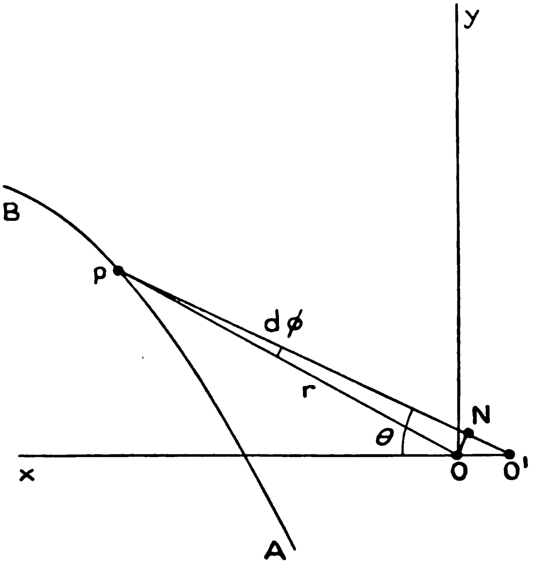
Let AB be the curve on the "table" and P the position of the tracing point upon it at any instant.

Let O be the position of the small wheel and Ox the direction of the tangent to the wheel at its point of contact with the drawing-board.

(The planes of the drawing-board and of the "table" are here treated as coinciding, instead of being parallel as they are in reality.)

The curve traced by the wheel upon the drawing-board will then have Ox as its tangent.

Fig. 1.



Let OO′ be a small element of this curve, and let the small angle OPO′ be denoted by $d\phi$.

Further, let the angle xO′P (which in the limit is equal to xOP) be denoted by θ and the length OP by r.

Let a perpendicular through O upon O′P meet the latter in the point N.

Then $O'N = dr$ and $ON = r\,d\phi$.

Thus

$$r\frac{d\phi}{dr} = \tan\theta.$$

Suppose now that the equation in polar coordinates of the curve on the "table" is

$$\tan\theta = rf(r),$$

where $f(r)$ is an arbitrary function of r; we have then

$$\frac{d\phi}{dr} = f(r),$$

and so $$\phi = \int f(r)\,dr + \text{constant}.$$

Since P is fixed with respect to the drawing-board, this is the polar equation of the curve traced by the wheel corresponding to the curve

$$\tan\theta = rf(r)$$

upon the "table."

It is to be observed in the figure that the angles θ and ϕ are measured in opposite senses.

Thus in order to integrate $f(r)$ with respect to r we trace the curve

$$\tan\theta = rf(r)$$

upon a piece of paper, which is then fixed to the "table" so that the origin is directly over the point of contact of the wheel and the direction from which the angle θ is measured lies in the plane of the wheel.

The "table" being now moved in such a way that the tracing point traverses this curve, the point of the paper on the drawing-board directly underneath the tracing point is determined, and then the angle between any two radii vectores from this point to the curve traced by the wheel gives the required integral between limits represented by the lengths of these two radii vectores.

The angle is measured by means of a protractor and expressed in radians.

Instead of using r as the independent variable, it is frequently better to employ $\log r$.

If $\log r = z$ we have

$$\frac{r\,d\phi}{dr} = \frac{d\phi}{dz} = \tan\theta.$$

If then we take the curve on the "table" of the form

$$\left.\begin{aligned} \tan\theta &= \mathrm{F}(z) \\ r &= e^{z} \end{aligned}\right\}$$

we have

$$\frac{d\phi}{dz} = \mathrm{F}(z),$$

and so $$\phi = \int \mathrm{F}(z)\,dz + \text{constant}.$$

There are two advantages in this.

In the first place we very frequently wish to obtain the integral of a function with the lower limit zero and our method ceases to give accurate results when r is small. If, however, we take z as the independent variable we avoid this difficulty; for since $r=e^z$, we may put $z=0$ and leave r with the finite value unity.

In the second place, provided we have a table of the exponential function, it is generally easier to trace the curve

$$\left.\begin{aligned} \tan\theta &= \mathrm{F}(z) \\ r &= e^z \end{aligned}\right\}$$

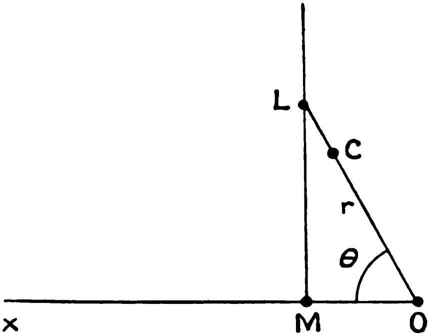
than it is to trace the curve

$$\tan\theta = r\,f(r),$$

since the latter involves multiplying the function to be integrated by the independent variable.

It is in fact practically as easy to plot the first of these curves upon squared paper as it is to plot $\mathrm{F}(z)$ in cartesian coordinates.

Fig. 2.



Thus taking O as origin and any convenient length OM as a unit we can measure lengths in this unit along a line through M perpendicular to Ox which are numerically equal to the values of $\tan\theta$.

Thus to plot the curve

$$\left.\begin{aligned} \tan\theta &= \mathrm{F}(z) \\ r &= e^z \end{aligned}\right\}$$

we select any value of z and take a point L in the perpendicular to Ox through M such that $\mathrm{ML}=\mathrm{F}(z)$ in the selected units.

Then $\mathrm{M\hat{O}L}=\theta$, and we have only to measure off a distance OC along OL such that $\mathrm{OC}=e^z=r$ in order to obtain a point C on the required curve.

If, on the other hand, we wished to plot the curve

$$\tan\theta = rf(r),$$

we should first select a value of r and take $\mathrm{ML} = rf(r)$ and then measure off a distance $\mathrm{OC} = r$ along the line OL. It is obvious in both cases that the unit in which r is measured along the radius vector need not necessarily be equal to OM, since we are only concerned with the ratio $\frac{\mathrm{ML}}{\mathrm{OM}}$. It is the unit in which r is measured along the radius vector which gives the scale of the curve.

In using the instrument it is important to know approximately how the "table" is to be rotated so as to keep the tracing point on the curve without pushing the wheel so that it moves sideways.

If a line $\mathrm{O}y$ be taken through O perpendicular to $\mathrm{O}x$, then it is easily seen that the centre of instantaneous rotation of the surface of the "table" lies at the intersection of $\mathrm{O}y$ with the normal to the curve at P.

When this is kept in mind the "table" can be moved in the proper way without difficulty.

The following figures show the degree of accuracy which may be obtained with such an instrument in integrating the functions $\int^r \frac{dr}{r}$ and $\int^r \frac{\sin r}{r}\,dr$:—

$$\int_1^r \frac{dr}{r}.$$

r.	ϕ in radians.	$\log_e r$ from tables.	Difference.
1	0	0	0
2	0·6836	0·6931	·0095
3	1·0908	1·0986	·0078
4	1·3788	1·3862	·0074
5	1·5999	1·6094	·0095
6	1·7831	1·7918	·0087

$$\int_0^r \frac{\sin r}{r}\,dr.$$

r.	$\phi + {}\cdot199$.	$\int_0^r \frac{\sin r}{r}\,dr$ from tables.
1·5	1·325	1·325
1·7	1·429	1·449
2·0	1·578	1·605
2·2	1·669	1·687
2·5	1·770	1·778
3·0	1·853	1·849

In the latter case a constant of integration ·199 was taken so as to make the result agree with the tables for $r = 1{\cdot}5$.

LXX. *Secondary Radiations produced by Gamma Rays and their Effect upon Gamma-Ray Absorption Measurements.*

By L. H. CLARK, *Ph.D.*[*], *M.Sc.*, *A.Inst.P.*, *The Physics Department*, *Middlesex Hospital*[†].

IN 1909, Tuomikoski[‡] investigated the absorption of gamma rays in lead and found that, as the thickness of lead was increased from 0·4 to 18 cm., the absorption coefficient decreased in value from 0·70 to 0·25 cm.$^{-1}$. Recently, many observers have studied the scattered radiation which all matter emits when irradiated by gamma rays, and Owen, Fleming, and Fage[§] have shown that it may play an important part in absorption measurements. The present investigation was made with a view to gaining more information about these scattered radiations and their effect upon gamma-ray absorption measurements. The experiments are divided into two groups. Those in the first group relate to a study of the radiation entering an electroscope suspended in enclosures of different substances when the direct beam of gamma rays to the former is heavily filtered by lead. In the second group, the effect of radiation scattered from the filters themselves upon absorption measurements is considered.

Fig. 1 is a scale diagram of the experimental arrangement. The electroscope was made of brass 0·065 cm. thick, and was spherical, measuring 2·2 cm. in diameter. It was suspended on a system of piano-wires, the rigidity of which was increased by a light wooden triangular framework D E F. A lead annulus 2·5 cm. in diameter and 0·18 cm. thick served to support the electroscope and a lead cap which covered the latter. The cap was a hollow cylinder of lead 0·18 cm. thick, closed at the top by a lead disk of the same thickness. Another cap of the same dimensions, but with a portion of the cylindrical side removable, was used for some experiments. When in use this cap, which is shown in fig. 1 A, was placed over the electroscope so that the removable portion, termed the window, faced the source of radiation. Measurements were made by timing the rate of fall of the gold-leaf of the electroscope, the case of which was earthed. The gold-leaf was charged by the movable wire C (fig. 1), which was put momentarily in contact with one pole of a constant voltage supply of 150–170 volts. During measurements, the wire C was earthed.

---

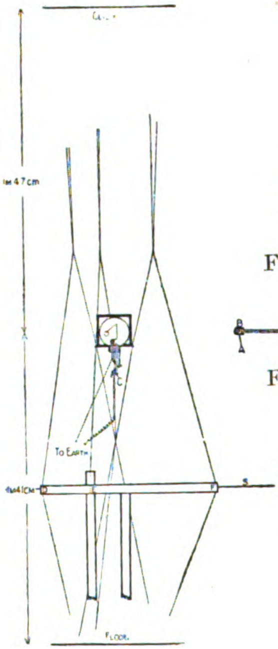
[*] Part of a Thesis submitted to the University of London for this Degree.

[†] Communicated by Prof. Sidney Russ, D.Sc.

[‡] Y. Tuomikoski, *Phys. Zeitschrift*, 1909, p. 372.

[§] A. E. Owen, N. Fleming, and W. E. Fage, Proc. Phys. Soc. xxxvi. 5, p. 355 (1924).

Fig. 1.



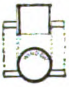


Fig. 1 A.

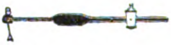


Fig. 1 B.

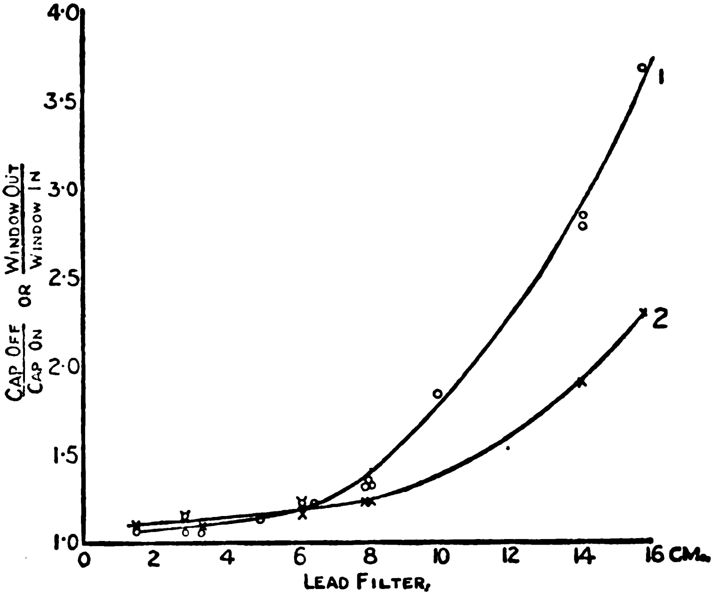
The sources of radiation were fairly large quantities of radium emanation. Fig. 1 B shows the glass vessel used to contain the emanation, so made that it could be filled repeatedly. The emanation was confined to the small bulb A, which was 0·5 cm. in external diameter, the remainder of the vessel being filled with mercury. The bulb A was covered by a small lead cap, the thicknesses of the closed end and sides of which were respectively 0·41 and 0·28 cm. In all the experiments the radiation was therefore first screened by this lead hood.

Group 1.

Preliminary experiments were made with the electroscope suspended mid-way between the floor and ceiling of the room

The radioactive source was set on a level with the centre of the electroscope, and the effect of covering the latter with the lead cap was determined. The ratio of the ionization readings, $\frac{\text{cap off}}{\text{cap on}}$, was 1·067 for distances between the source and the electroscope ranging from 9 cm. to 28 cm. When lead filters were interposed in the primary beam, the ratio $\frac{\text{cap off}}{\text{cap on}}$ was found to increase with the thickness of the former in the manner shown by the curve 1 of fig. 2.

Fig. 2.



The filters were mainly cylinders varying in diameter from 2·37 to 3·55 cm., and the distance of the source from the electroscope ranged from 9 cm. to 28 cm. The curve shows that as the thickness of the filter is increased, the radiation entering the electroscope becomes softer, the change in quality being most marked for filters over 8 cm. thick.

A similar series of measurements was made with the lead cap shown in fig. 1 A. In this case, the major portion of the cap covered the electroscope throughout the experiment, and the ratio $\frac{\text{window out}}{\text{window in}}$ was obtained for lead filters of different thickness. The variation of this ratio with the thickness of the filter is shown by curve 2 of fig. 2. A comparison of curves 1 and 2 shows that the effect of surrounding the major portion of the electroscope with the second cap is to decrease the quantity of soft radiation entering the electroscope. One may conclude, therefore, that the soft radiation is scattered mainly from the surroundings in which the measurements are made.

Experiments were then made to determine how the quality of the scattered radiation varied with the surroundings in which the measurements were made. The procedure was as follows:—

A series of enclosures of equal internal volume but having walls of different substances were built in turn around the electroscope and source. For this purpose the light wooden framework shown in fig. 3 was erected around the apparatus. Surrounds of aluminium, zinc, lead, 3-ply wood, paraffin wax, and brick were made by covering the sides of the framework with the different substances. The direct beam of gamma rays to the electroscope was practically eliminated by a cylindrical lead filter 15·86 cm. long and 3 cm. in diameter. The distance between the source and the centre of the electroscope was maintained approximately 20 cm. The quality of the radiation entering the electroscope was measured by the ratio $\frac{\text{cap off}}{\text{cap on}}$.

Fig. 3.

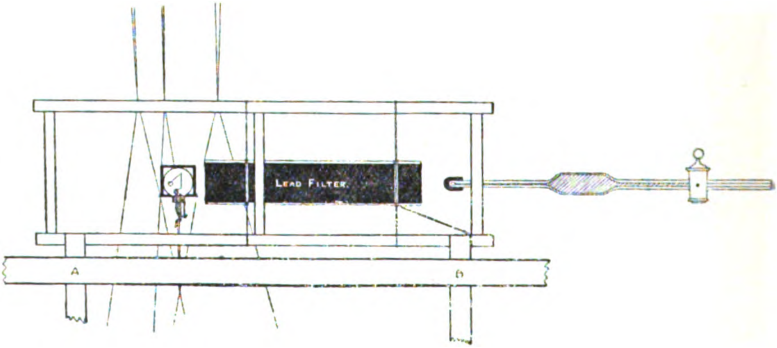


Table I. gives the results obtained with the different enclosures and includes the values found when the wooden framework was left bare so that the room formed the surround.

TABLE I.

Surround.	Wall thickness.	% Absorption. Primary γ rays.	Cap off. Corrected reading.	$\frac{\text{Cap off}}{\text{Cap on}}$.
Room	—	—	1·46	4·34
Aluminium	0·013 cm.	—	1·63	5·49
Zinc	0·023 ,,	0·6	2·56	4·28
3-ply Wood	0·50 ,,	—	2·65	3·54
Lead	0·18 ,,	8·0	5·08	3·18
Paraffin Wax ...	2·7 ,,	6·2	7·39	3·37
Brick..............	6·4 ,,	29·7	28·0	4·93

The ratio $\frac{\text{cap off}}{\text{cap on}}$ for the different surrounds shows no marked variations, but the "cap off" readings differ considerably among themselves. The thickness of the enclosure wall varied from one substance to another, and a comparison of the figures in columns 3 and 4 shows that the largest "cap off" readings were obtained with those surrounds, the walls of which absorbed the largest quantities of primary gamma radiation. This is further shown by the figures in Table II.,

TABLE II.

Lead Surround.	Ionization Readings.		$\frac{\text{Cap off}}{\text{Cap on}}$.
	Cap off.	Cap on.	
0·17 cm.	4·23	1·38	3·06
0·33 ,,	4·56	1·7	2·68
0·66 ,,	4·99	2·0	2·49

which were obtained for lead enclosures of equal internal volume but differing in wall thickness. This Table shows in addition that the scattered radiation from the lead enclosure becomes more penetrating as the thickness of the walls is increased.

To compare the quality of the radiation scattered from different substances, the above results indicate that thicknesses of the various substances should be chosen which are equivalent in absorbing power for the primary gamma rays. The ratio $\frac{\text{cap off}}{\text{cap on}}$ for enclosures having equivalent wall-thicknesses of lead and of brick of 0·66 and 6·4 cm. were respectively 2·49 and 4·93 cm.$^{-1}$. The coefficients of absorption in lead of these scattered rays are respectively 5·06 and 8·85 cm.$^{-1}$. Assuming Owen's law, viz. $\mu \propto \lambda^3$, where μ and λ have their usual significance, it can be shown that $\frac{\lambda \text{ brick}}{\lambda \text{ lead}} = 1{\cdot}2$. The internal volume of the brick surround was approximately 38 per cent. larger than that of the lead enclosure. Subsequent experiments show that the difference in wave-lengths of the scattered radiations from brick and lead surrounds of equal internal volume would be less than 20 per cent. These scattered radiations have wave-lengths approximating to those of X-rays excited by a peak potential of 196,000 volts, for which Rutherford[*] found a mass absorption coefficient of 0·75 corresponding to a wave-length of 0·063 Å unit. Hull found that $\frac{\mu}{\rho}$ for the K characteristic radiation of lead in lead was 1·51, denoting a less penetrating radiation than the observed scattered radiation.

The above results are in general agreement with those of Compton[†], who showed by a different method that matter irradiated by gamma rays emits a softer radiation, the wave-length of the softest components of which lay between 0·06 and 0·12 Å unit.

A number of enclosures of different internal volume having walls of the same material and thickness were then built around the electroscope, and the quality of the radiation scattered from each was measured in the manner of the last experiment. Table III. gives the results obtained with brick enclosures.

This material was chosen so that the surrounds would consist of approximately the same substance as the walls of the room. The figures within brackets in the first column

---

[*] E. Rutherford, Phil. Mag. xxxiv. p. 153 (1917).

[†] A. H. Compton, Phil. Mag. xli. p. 749 (1921).

TABLE III.

Brick Surround.		Distance Source – Electroscope.	Ionization Readings.		$\frac{\text{Cap off}}{\text{Cap on}}$.
Number of Bricks.	Internal Volume.		Cap off.	Cap on.	
12	6·28 litres	19·9	20·3	3·96	5·12
42	42·6 ,,	,,	23·7	3·12	7·6
Room	—	,,	1·4		
12	6·28 ,,	19·8	15·9	3·23	4·93
Room	—	—	0·80		
19	7·74 ,,	20·7	8·82	1·44	6·12
31	24·8 ,,	—	9·46	1·37	6·9
26	26·3 ,,	21·2	19·0	2·82	6·74
49	75·0 ,,	20·5	20·9	2·1	9·83

were obtained on the same day with the same source, so that the ionization readings thus bracketed may be compared. For these, it is seen that the "cap off" readings increase but the "cap on" readings diminish with increase in the size of the enclosure. The ratio $\frac{\text{cap off}}{\text{cap on}}$ thus increases considerably as the enclosure is enlarged.

TABLE IV.

Surround.	Distance Source – Electroscope.	Ionization Readings.		$\frac{\text{Cap off}}{\text{Cap on}}$.
		Cap off.	Cap on.	
Large Lead ...	20·0	5·48	0·85	6·45
Small Lead ...	19·8	5·08	1·6	3·18
Room............	,,	1·33		

The results given in Table IV. lead to similar conclusions. They were obtained when the apparatus was surrounded by lead enclosures of wall thickness 0·18 cm. The internal volumes of the large and small enclosures were respectively 55·5 × 44 × 44 cm. and 11 × 12 × 34·5 cm.

A consideration of the above results shows that the change in volume of a lead surround required to double the ratio $\frac{\text{cap off}}{\text{cap on}}$ is approximately twice that necessary to produce the same change with brick enclosures. These facts indicate that the radiation entering the electroscope is complex. If a single scattered radiation from the walls of the enclosures was present, one would expect that both the "cap off" and "cap on" readings would diminish as the surround was enlarged, and not as has been found. The increase in the ratio $\frac{\text{cap off}}{\text{cap on}}$ with increase in the size of the surround, and therefore with the quantity of air enclosed by the latter, suggests the presence of a scattered radiation from the air which is softer than that from the walls of the enclosure. Experiment has shown that the radiation scattered from a brick surround is softer than that from one of approximately the same size of lead 0·18 cm. thick, the ratio $\frac{\text{cap off}}{\text{cap on}}$ for the former being 1·55 times that for the latter. Moreover, it has been seen that the quantity of scattered radiation is intimately related to the amount of primary radiation absorbed in the scattering substance. Assuming the presence of a scattered radiation from the air, one would expect therefore that, in order to decrease the penetrating power of the radiation entering the electroscope by a given amount, the necessary change in volume for the lead surround must be greater than that for the brick enclosure. The experimental data support this conclusion.

GROUP 2.

In this section, some experiments are recorded showing the effect of radiation scattered from the filter upon gamma-ray absorption measurements.

Conical lead filters were made of varying length having apex angles equal to the cone of rays from the source which just enveloped the bulb electroscope in the particular experiments. The amount of radiation scattered from the filter would thus be reduced to a minimum, and one would expect that lower transmission values than those of Tuomikoski* would be obtained. From the figures given in Table V., however, it is seen that the values of Tuomikoski are in all cases lower. This result indicates, therefore, that the amount of scattered radiation from the surroundings which entered the electroscope was greater than in Tuomikoski's experiment.

---

* *Loc. cit.*

TABLE V.

Cone Thickness. cm.	Transmission. per cent.	Tuomikoski's Values.
1·33	43·4	42·9
1·45	3·34	3·17
7·08	2·52	2·51
7·95	2·02	1·50

A comparison of the ionization readings obtained with two cylindrical filters 14·0 and 14·1 cm. long, the respective cross-sections of which were in the ratio of 1·5 to 1, showed that the readings for the filter of smaller diameter was the larger by 24 per cent. For two lead filters 6·7 cm. thick, one having a cross-section 25 times the other, the ionization readings differed by 22 per cent., the larger reading in this case being obtained with the filter of larger cross-section.

It has been shown in the first section of the paper that the effect of radiations scattered from the surroundings may be considerable. An increase in the cross-sectional area of a filter will increase the quantity of radiation scattered from the filter but will diminish the amount of scattered radiation from the surroundings which enters the electroscope.

The variation in the apparent transmission of gamma rays through comparatively thin filters with their disposition between the source and the electroscope was then measured. Ionization readings were taken with (*a*) the filter near the electroscope—the A position, (*b*) the filter near the source—the B position, and (*c*) no filter. This experiment was made with cylindrical filters, 3 cm. in diameter, of silver, lead, and platinum. The thickness and mass of each was as follows:—

	Thickness.	Mass.
Silver . . .	1·55 cm.	113·8 gms.
Lead . . .	1·45 „	111·5 „
Platinum . .	0·75 „	112·2 „

The results obtained with the respective filters are given in Table VI.

TABLE VI.

Filter.		Distance from Electroscope to Filter. cm.		Percentage Transmission.	
Element.	Thickness, cm.	A Position.	B Position.	A Position.	B Position.
Silver.........	1·55	2·5	26·2	48·3	55·4
Lead	1·43	,,	,,	42·1	45·6
Platinum ..	0·75	,,	,,	41·9	45·2

The apparent transmission of each filter is greater when it is placed near the source than when near the electroscope, a result previously obtained by Florance *, who used lead filters. For lead and platinum cylinders, the difference in the apparent transmission was approximately 8 per cent., but that for the silver one amounted to nearly 15 per cent. To determine the cause of this variation, the further experiment was made of comparing the transmission of a lead filter placed in the A position with that of another of the same thickness but of smaller cross-section placed in the B position.

Fig. 4.

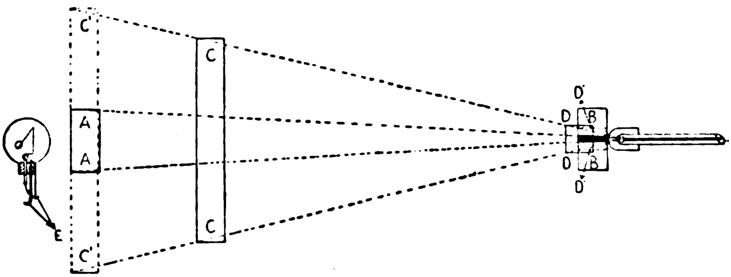


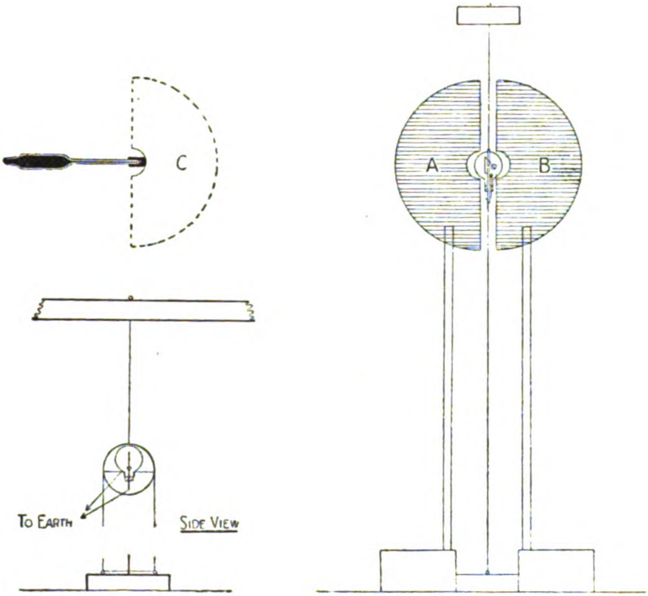
Fig. 4 is a scale diagram of the experimental arrangement, where C and D represent the filters so placed that C coincided with the shadow of D thrown by the source, the area of C being 57·3 times that of D. Each filter thus received practically the same quantity of gamma rays. The apparent transmission of the larger filter was 8·8 per cent. bigger than that of the smaller one, which may be attributed to the

---

* D. C. H. Florance, Phil. Mag. ii. p. 921 (1910).

excess of scattered radiation from C, which subtended a bigger solid angle at the electroscope than D. It is safe to assume that the difference would be greater for two similar filters in the dotted positions C′ and D′, the areas of which would be in the ratio of 135 to 1. These dotted positions coincide with the two positions A and B of the silver, lead, and platinum cylinders used in the former experiment. The difference between the apparent transmission of the cylindrical lead filter A and the small shaded portion of it in the B position, would be less than that between the filters C′ and D′. The effect of the whole lead cylinder B, the area of which is 73 times that of the small shaded portion, will make the apparent transmission of the filter in this position greater than when the same filter is placed at A. One may conclude therefore that a given filter becomes a more powerful source of scattered radiation the nearer it is placed to the source of primary gamma rays, and consequently appears more transparent in this position.

Fig. 5.



A study was then made of the radiation scattered from filters of paraffin wax. For this purpose a suspended silver sphere electroscope was used to measure the radiation transmitted by wax filters which were hemispherical. The experimental arrangement is shown in fig. 5.

The electroscope was 2·57 cm. in diameter and its wall-thickness 0·0158 cm. The diameters of the filters were respectively 16·3, 10·0, 7·8, and 5·2 cm., each filter being made in duplicate. The radon source used in former experiments was set up at a distance of 33 cm. from the centre of the electroscope. Readings were taken under the following conditions :—

(1) Without wax.
(2) With a paraffin hemisphere in the position A.
(3) With a wax sphere A, B surrounding the electroscope.
(4) With a wax hemisphere in the dotted position C.

Table VII. shows the results obtained.

TABLE VII.

Sphere and Hemisphere. Diameter, cm.	% Transmission.		% Transmission.	
	Hemisphere.	Sphere.	Without Lead.	With Lead.
0	—	—	—	91·0
5·2	99·1	100·	103·8	84·2
7·8	95·5	101·	101	83·0
10·0	94·1	100·5	100·7	81·6
16·3	94·4	107·8	103·8	79·0

The apparent transmission of the filters in the A and C positions are given respectively in columns 2 and 4. The apparent transmission of a wax cylinder 3 cm. in diameter and 7·0 cm. long, which was equivalent in thickness to the largest hemisphere, was 69·3 per cent. when placed in the C position. The corresponding figure for the largest hemisphere was 103·8 per cent. It is clear, therefore, that much of the ionization recorded with the wax hemispheres is due to radiations scattered from them. Moreover, the figures in column 4 indicate that the amount of this scattered radiation increases with the size of the hemisphere. This fact is further illustrated by the figures in column 3, which were obtained when the electroscope was enclosed in turn by wax spheres of increasing diameter.

The quality of the radiation transmitted by the hemispheres placed in the C position was then compared with that of the primary rays. A lead sheet measuring 12 × 14·4

× 0·16 cm. was mounted vertically at a distance of 4·5 cm. from the electroscope, and its transparency was found for (*a*) the primary rays, (*b*) the rays transmitted by the wax hemispheres. The results thus obtained are shown in the last column of Table VII. The transmission of the lead sheet is seen to decrease with increase in the diameter of the hemisphere, showing that as the size of the latter is increased, the radiation entering the electroscope becomes softer. With the wax cylinder filtering the primary beam, the lead sheet transmitted 90·3 per cent. of the radiation incident upon it. One may conclude that the softening of the radiation with increase in the diameter of the wax hemisphere is due to the increase in the amount of scattered rays, which are softer than the primary gamma radiation. The quality of this scattered radiation may be determined as follows:—The difference in the ionization readings obtained with the largest hemisphere and cylinder was 2·65 div./min., which fell to 1·38 div./min. when the lead sheet was interposed. The absorption coefficient in lead calculated from these figures is 4·06 cm.$^{-1}$, which is of the same order as those obtained for the radiations scattered from the enclosures described in Part I. of this paper.

CONCLUSION.

Absorption measurements made with an electroscope suspended in air show the presence of a general scattered radiation from the surroundings which may contribute more to the ionization than the radiation transmitted by very thick lead filters. This scattered radiation is considerably softer than the primary rays which provoke it. A study of the radiations scattered from different substances irradiated by the same beam of gamma rays reveals the following facts:—

(1) The penetrating power of the radiation scattered from layers of lead up to 0·66 cm. thick increases with the thickness of the layer.

(2) The radiations scattered from layers of different substances which are equally absorbent for the primary gamma rays have a wave-length of about 0·063 Å unit, corresponding to X-rays excited by a peak potential of 196,000 volts.

Experimental evidence has been obtained of a comparatively soft radiation scattered from air irradiated by gamma rays.

To avoid errors in absorption measurements due to scattered radiations, it is suggested that use should be made of the fact that they are comparatively soft. A lead filter 1·0 cm. thick absorbs nearly 99 per cent. of the hardest scattered radiation dealt with in the above experiments, and the use of an electroscope having walls of this material and thickness would practically eliminate errors due to this cause.

I thank the Medical Research Council for the use of large quantities of radium emanation and for facilities to carry out some of the experiments. To Mr. Spicer, of the Radon Department of the Middlesex Hospital, I am indebted for the preparation of the radon sources.

The experiments were made at the instigation of Professor Russ, and I thank him warmly for the help and valuable suggestions he has given me.

LXXI. *The High Vacuum Arc in Hydrogen.* *By* F. H. Newman, *D.Sc., A.R.C.S, Professor of Physics, University College of the South-West of England, Exeter* [*].

[Plate XV.]

In a previous paper [†] it has been shown that with metallic sodium as the cathode an arc in hydrogen gas at low pressure can be started and maintained between cold electrodes with comparatively small applied potential differences. At very low gas pressures, *i. e.* before the heat from the arc vaporized the sodium to any appreciable extent, the glass walls of the containing tube showing the green fluorescence under the electric discharge action, the radiation from the arc consisted mainly of the secondary and Balmer series hydrogen lines, the brightest lines being those which constitute the first Fulcher bands in the red. It is well known that high relative intensity of the secondary lines appears under less energetic conditions of excitation and, in particular, the Fulcher bands are developed at low potentials. This type of arc differs from the normal arc in that its cathode is not incandescent or even hot, and therefore thermionic electrons are not supplied continuously in great abundance at the negative pole. Under normal conditions the arc is most difficult to start, and is most intermittent, when formed between metal electrodes which conduct heat well. It is also difficult to maintain in hydrogen, this gas having a higher thermal conductivity than air. In the case of the normal arc the cathode is presumably maintained in the high temperature condition by the collisions on it of positive ions which have been subjected to the cathode potential fall. With cold electrodes other processes must supply the electrons necessary for the arc maintenance. The atoms of the gas, which are in the metastable condition as the result of collisions with electrons, will on returning to the normal state emit radiant energy which may strike the cathode, be absorbed by it, and cause electrons to flow from the cathode. Electrons are also emitted from a cold plate bombarded with positive ions and, in addition, positive ions flowing rapidly across a gas ionize some of the atoms in it. These latter processes, however, are inefficient at the low speeds with which the ions move under low potential differences. Recently Thomson * has pointed out that there are, probably, several types of radiation near the cathode of an electric discharge-tube, and similar radiations may arise within the cathode fall of potential in the arc.

---

[*] Communicated by the Author.

[†] Phil. Mag. i. p. 940 (1926).

In the present experiments the vacuum arc tube was similar to that used previously, but an iron electrode was substituted for the sodium cathode, so that the arc was struck and maintained between iron electrodes which were distant apart 2 cm. A momentary electric discharge could be passed between one of these arc electrodes and a third one inserted in the tube. This initial discharge was necessary to strike the arc. The radiation was viewed and photographed by means of a quartz spectrograph through a quartz window.

At first the tube was exhausted continuously to a pressure of 10^{-4} mm. of mercury, the residual gases consisting chiefly of oxygen, nitrogen, hydrogen, water vapour, and the carbon oxides. Applying 80 volts across the arc electrodes, and passing an electric discharge through the tube by means of a coil, a brilliant arc through the residual gases was obtained. The arc persisted after the electric discharge from the coil was stopped. The radiation was nearly white in colour, and when examined was found to consist chiefly of the Balmer and secondary hydrogen lines together with a continuous

---

* Phil. Mag. xlviii. p. 1 (1924).

spectrum throughout the range λ 6000–λ 2000. The nitrogen bands were faint, but the ammonia bands λ 3360, λ 3371 were prominent. The current could be varied between 6 and 10 amperes by means of a rheostat, but at the higher currents the tube soon fractured owing to the intense heat generated. The formation of such an arc is interesting and was unexpected because the ordinary electric discharge passed through the tube with difficulty and there had been no sign of luminosity, the tube walls fluorescing under the cathode ray action. This arc persisted for about a minute. Although the cathode became very hot there was no trace of iron lines in the radiation, so that there does not appear to be any appreciable vaporization of the iron electrodes. The intense heat generated by the arc liberated gases occluded within the glass walls, and if these gases were not removed rapidly the gas pressure rose to such a high value that the arc was extinguished.

Occasionally a brilliant white glow was formed between the arc electrodes. It was momentary, and was certainly not the typical arc. The electrodes remained cold while this glow existed and no occluded gas appeared. It was impossible to produce the glow in the absence of the potential difference across the arc electrodes, in fact the ordinary electric discharge from the coil gave no luminosity within the tube owing to the low gas pressure. The glow spectrum resembled that of the arc, although with the latter the secondary hydrogen lines were relatively brighter than the Balmer lines. This is shown in spectrograms Nos. I and II (Pl. XV).

In a second series of experiments a stream of hydrogen generated by the electrolysis of a phosphorus pentoxide solution was passed through the tube for several hours to eliminate, as far as possible, all gases except hydrogen and water vapour. With the gas at a pressure of 10^{-2} mm. of mercury an arc similar to that described above could be started and maintained at low potential differences between the arc electrodes. The cathode became very hot, almost incandescent, but there was no trace of iron lines in the spectra of the emitted radiation. In some experiments the current was 10 amperes, but the actual fall of potential across the electrodes was never less than 40 volts. Such an arc in hydrogen at the voltages in the absence of an incandescent cathode is unusual.

The arc would strike with the gas pressure at 10^{-1} mm. of mercury if the iron electrodes were clean and bright, but after the first flash had been extinguished it was very difficult to restart the arc unless the electrodes were removed and the surfaces cleaned. A probable explanation of this is the formation of an iron-oxide film on the electrodes. Oxygen liberated from the dissociated water vapour, which was always present, acts on the iron forming the oxide. This film would increase the cathode fall.

Both the arc and glow in hydrogen could be obtained at pressures below 10^{-8} mm. of mercury, and although the spectra of the radiation in the two phenomena were similar, the arc spectrograms indicated more continuous spectrum than those of the glow, and the water bands in the ultraviolet were more prominent in the glow radiation. Greater relative intensity of the Balmer lines and disappearance of the continuous spectrum were associated with prominent water bands, as shown in spectrograms Nos. III, IV, V (Pl. XV.).

The initial ionization of the gas molecules when this high density current arc is started must be produced indirectly by the cathode rays. As pointed out by Thomson *, the source of ionization in the Crookes' dark space is not due wholly or mainly to the detachment of electrons from gas molecules by collision. In the present experiments the dark space extended throughout the tube, and it is probable that the ionization of the gas molecules is brought about by high-frequency radiation from those gas molecules which have been subjected to collisions with cathode rays. These collisions do not result in the splitting off of electrons, but the electrons in the inner layers of the molecules are displaced without ejection from the molecule. The return of these electrons to their old positions would be accompanied by the emission of high-frequency radiation which could ionize molecules on which it fell. The recombination of the ions produces the glow, and the absence of any strong field, *i. e.* when the coil discharge ceases, allows such recombinations, the gas glows and finally arcs.

---

* *Loc. cit.*

LXXII. *On the Action in Parabolic Paths under Gravity.*

By W. B. MORTON, *M.A., Queen's University, Belfast* *.

A CERTAIN amount of what may be called arithmetical vagueness is attached to the Principle of Least Action owing to the lack of numerical values for the magnitude in question. Analytical expressions for the Action can be found in simple cases of free paths, but in order to illustrate the stationary property possessed by such values one would like to follow the variation of the Action when the free path is gradually deformed, in some definite way, into adjacent guided paths. I have done this for the parabolic trajectory under gravity, between two points at the same level, the varied paths being also parabolic. The action between two points on a guided parabolic path with axis vertical, can be expressed by means of elliptic functions. The results have perhaps some interest as illustrating the Principle of Least Action and also a point in the calculus of variations.

A particle is projected along a smooth tube, or a bead along a smooth wire, in the form of a parabola with axis vertical and vertex upwards. Let c be the height of the level of no velocity above the vertex of the parabola $y^2=4ax$, then the action between the ends of a horizontal chord is

$$\mathrm{A}=2\sqrt{(2g)}\int_0^x(x+c)^{\frac{1}{2}}\,.\,(x+a)^{\frac{1}{2}}\,.\,x^{-\frac{1}{2}}dx.$$

This is an algebraic function of x in two cases:

(1) when $c=a$ and the path is a free trajectory,

$$\mathrm{A}=\frac{4}{3}\sqrt{(2g)}x^{\frac{1}{2}}(x+3a)\ ;$$

(2) when $c=0$ and the path touches the level of no velocity,

$$\mathrm{A}=\frac{4}{3}\sqrt{(2g)}(x^{3/2}-a^{3/2}).$$

In other cases A is expressed by elliptic functions.

Suppose $c>a$, then the substitution

$$x=a\,sc^2u \text{ with } k^2=(c-a)/c$$

transforms the integral into

$$2ac^{\frac{1}{2}}\int^u dn^2u\,.\,nc^4u\,.\,du=\frac{2}{3}ac^{\frac{1}{2}}\{snu\,.\,dnu\,.\,nc^3u$$
$$+2u+(2-k^2)(snu\,.\,dnu\,.\,ncu-\mathrm{E}u)/k'^2\}.$$

---

* Communicated by the Author.

The case when $c<a$ is met by interchange of letters c, a. If it is desired to include paths lying below the horizontal with the vertex of the parabola downwards, the action is

$$2\sqrt{(2g)}\int_0^x (c-x)^{\frac{1}{2}} . (x+a)^{\frac{1}{2}} . x^{-\frac{1}{2}}dx.$$

The substitution $x=c\,cn^2 u$ with $k^2=c/(a+c)$ gives for the above integral the expression

$$2c(a+c)^{\frac{1}{2}}\int sn^2u\,.\,dn^2u\,.\,du$$

$$=2c(a+c)^{\frac{1}{2}}\{k'^2u-k^2snu\,.\,cnu\,.\,dnu+(2k^2-1)\mathrm{E}u\}/3k^2.$$

For comparison with these parabolic paths we may include the action along paths made up of two vertical lines connected by a horizontal line at their upper ends. If the initial upward velocity is that due to height h, the height of the horizontal part of the path z, and the horizontal range r, then

$$\mathrm{A}=\sqrt{(2g)}\left\{2\int_0^z (h-x)^{\frac{1}{2}}dx+(h-z)^{\frac{1}{2}}r\right\}$$

$$=\frac{4}{3}\sqrt{(2g)}\left\{h^{3/2}-(h-z)^{3/2}+\frac{3}{4}(h-z)^{\frac{1}{2}}r\right\}$$

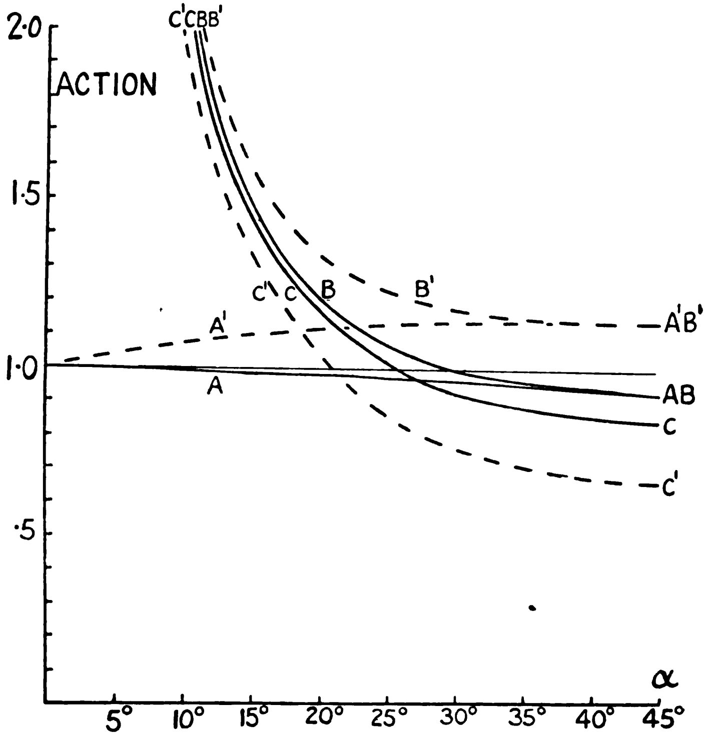
with the limiting value $\frac{4}{3}\sqrt{(2gh^3)}$.

It is convenient to take as unit of action the value for the direct passage at constant velocity along the horizontal range. This is $4\sqrt{(2gax\,.\,c+x)}$ in the parabolic, and $\sqrt{(2gh)}r$ in the rectangular paths.

With a given velocity of projection $\sqrt{(2gh)}$ each horizontal range r, inside the maximum $2h$, can be reached with a pair of complementary angles of elevation $\left(\alpha, \frac{\pi}{2}-\alpha\right)$. We shall take $\alpha<\frac{1}{4}\pi$. Then $r=2h\sin 2\alpha$. The two trajectories may be distinguished as the lower and upper free paths. Their vertices are at heights $h\sin^2\alpha$, $h\cos^2\alpha$, and their parameters are $h\cos^2\alpha$, $h\sin^2\alpha$, respectively. The formulæ given above enable us to calculate, without elliptic functions, the values of the action for three special parabolic paths, viz., the two free paths and the "limiting parabola" which touches the level of no velocity, and for three rectangular paths whose horizontal portions are at the level of the vertices of the three parabolas.

The results are plotted (fig. 1) against the angles of elevation, the unit in each case being the horizontal action for the corresponding range. The full lines are for the parabolas, and the broken lines for the rectilinear paths. Curve A shows the action for the lower trajectory, B for the upper, and C for the parabola which rises to the level of no velocity. A′B′C′ are for the corresponding rectangular paths.

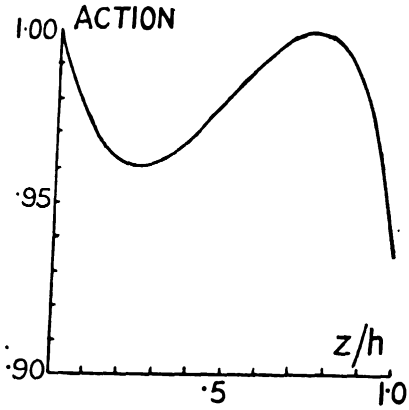
Fig. 1.



Let now a particular range be taken, and let a series of parabolas be drawn with vertices at heights ranging from zero to *h*. The parabolas which lie below the lower and above the upper free paths have their directrices above the level of no velocity ($a > c$), those between the two free paths have their directrices below this level ($a < c$). It is known that the action along the lower trajectory is a true minimum because the end of the path is reached before the point where the path touches the parabolic envelope of all the parabolas which can be described from the initial point with the same velocity of projection. This point, the "kinetic focus," is at the other end of the chord drawn from the point of projection to the focus. For the upper trajectory, on the other hand, the kinetic focus is passed during the flight and the action is a minimum for some ways of deforming the path but a maximum for others.

The calculation of the formula involving elliptic functions has been carried for the case $\alpha=30°$. The modular angle was given a series of values, multiples of 5°, and the action tabulated against z/h, the height of the vertex expressed as a fraction of the velocity-head. The result is shown on fig. 2.

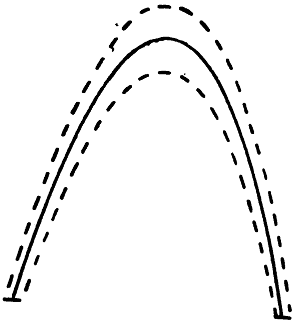
Fig. 2.



It will be seen from fig. 1 that for this special value of α the action along the upper trajectory is equal to that along the horizontal range which has been taken as unit. It appears that for this kind of variation there is a maximum value of the action along this free path. The minimum action along the lower trajectory is only about 4 per cent. less than this, so the ordinate has been plotted on a large scale beginning from the value ·90.

One would like to complete the illustration of the difference between the two kinds of free path by devising some other way of gradually varying the curves which would give minimum action for the upper trajectory also. A way which suggests itself, and which retains the parabolic form, is to lower or raise the free path without changing it otherwise, introducing horizontal straight pieces at the ends to complete the journey (fig. 3). Beginning with either free path we may depress the vertex down to the horizontal range or raise it to the level of no velocity. There is a fundamental difference, however, between this way of changing the path and the previous one. No matter how close the changed path is to the free trajectory, it is not a "slightly varied path" in the meaning of the calculus of variations. In the procedure of that calculus it is assumed that not only the ordinate but also the slope of the curve is varied continuously, that both δy and $\delta(dy/dx)$ are small quantities of the first order. The latter condition is not fulfilled at the ends of the curve in the present case, and, in consequence, the change in the action is of the first instead of the second order. Notwithstanding this, the action along either free path possesses the minimum property, in the sense that it increases when we pass to the changed path on either side. If the vertex of the parabola is raised by δz, the action is increased by

Fig. 3.



$$\sqrt{}(2ga/x)\{(x+a)^{\frac{1}{2}}+a^{\frac{1}{2}}\}\delta z\ ;$$

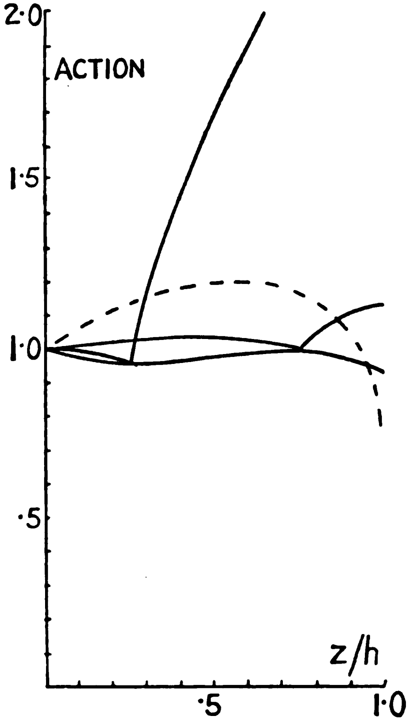
if it is lowered, there is again an increase of

$$\sqrt{}(2ga/x)\{(x+a)^{\frac{1}{2}}-a^{\frac{1}{2}}\}\delta z.$$

The discontinuity is, of course, due to the fact that the contributions of the little straight pieces are always positive. To get analytical continuity in the values they should change sign in passing from one side to the other of the end-points.

These results are shown on fig. 4. The action graph of fig. 2 is plotted on one-tenth the scale, and from its minimum and maximum there spring pairs of curves showing the action for the discontinuous paths. The broken line has been added to show the action along the upward and downward verticals connected by a horizontal line at level z. This has a maximum value when $z=h-\frac{1}{4}r$ when, in terms of the unit adopted,

Fig. 4.



$$A=\frac{4}{3}(h/r)+\frac{1}{3}\surd(r/h).$$

In the present case $r=h\sqrt{3}$, which gives for the maximum

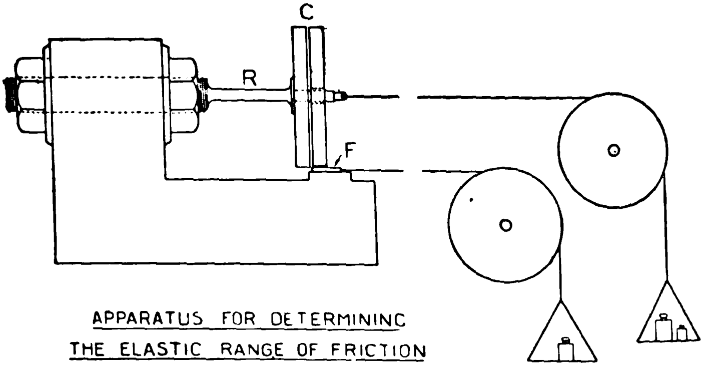
$$z/h=\cdot 567,$$

$$A=1\cdot 209.$$

LXXIII. *The Elastic Range of Friction.* *By* JAMES S. RANKIN, *B.Sc., A.R.T.C., Lecturer, The Royal Technical College, Glasgow* *.

IN a paper on "Molecular Contact" by James S. Stevens, published in the 'Physical Review' for 1899, it is shown (by an interferometer method) that when one metal plate is pulled over the surface of another, as in an ordinary experiment for finding coefficients of friction, then, before slipping occurs, *elastic* strains are produced of magnitudes one or two tenths of a wave-length of yellow light ($\lambda = \cdot 00006$ cm.). It was thought that a further investigation of this elastic range of friction, using an oscillating-valve ultramicrometer method capable of detecting say 10^{-7} cm.†, might lead to a better understanding of the nature and distribution of ordinary friction and of the action of the surface films concerned.

Fig. 1.



The apparatus first employed is illustrated by figs. 1 and 2. A parallel plate condenser C, formed of two metal plates (7 cm. × $2\frac{1}{2}$ cm.) with surfaces say 1/20 mm. apart, was placed in an oscillating electric circuit (frequency of the order one million per second) connected to the grid of a thermionic valve. A second valve was provided with a similar grid circuit having a variable condenser, so that its frequency could be adjusted to say 1 million 200 per second. The high-frequency currents in the plate or sheath circuits of these two oscillating valves, acting on ear telephones, gave rise, due to interference, to an audible note in the telephones of beat frequency about 200 per second. An alteration of the capacity of the condenser C, produced by a change in the distance between the plates of say 10^{-7} cm. caused the frequency of the note heard in the telephones to alter in a manner which could readily be recognized by the ear.

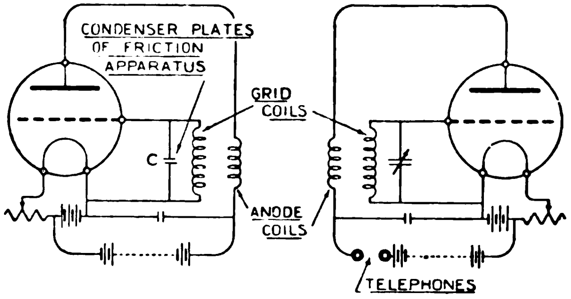
---

* Communicated by the Author.

† Whiddington, Phil. Mag. Nov. 1920. He detected 5×10^{-9} cm.

One of the plates of the condenser C—the right-hand plate which had a hole drilled in its centre—was fixed to the top of the thin plate F; the friction at the under surface of F being the subject of investigation. The other plate of the condenser C was attached to a carefully measured standard steel rod R fixed to a rigid support; the dimensions of the rod were such that a pull of 100 grams extended it by 10^{-6} cm. The apparatus was enclosed in a lead-lined box to avoid electric induction effects and placed on a firm foundation to avoid vibration.

Fig. 2.

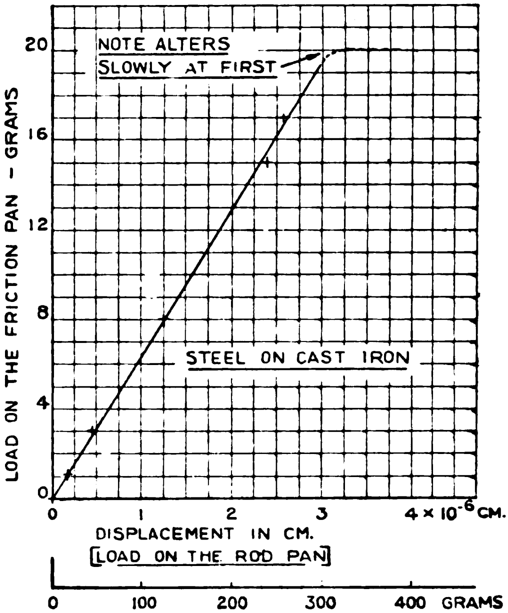


OSCILLATING VALVE CIRCUITS FOR FRICTION APPARATUS

A tangential pull (of say 10 grams weight) applied to the plate F slightly increased the distance between the plates of the condenser C; a pull (of say 200 grams) applied to the rod R decreased this distance by about the same amount. The elastic yield at the friction surfaces could thus be measured by the elastic yield of the standard rod R—the equality of the two strains being detected by the change in the frequency of the note heard in the telephones, as loads were lifted off and on. The rigidity of the supports was tested by applying pulls to various points other than the end of the rod R or the friction plate F.

Figure 3 shows the results obtained using as friction surfaces steel against cast iron. The elastic range of friction is clearly shown, and the "yield-point" on the graph when limiting friction was reached at the pull of 20 grams was fairly accurately determined by the manner in which the note heard in the telephones *slowly* altered after the pull was applied.

Fig. 3.



The effect produced by adding additional normal load to the friction plate F, such that the normal reaction between the surfaces was doubled (160 grams instead of 80), was also tested with the same two surfaces; and the experiments indicated that the elastic modulus for friction was thereby about doubled. For example, 10 grams pull on the friction plate now produced only about one-half the elastic yield previously observed: limiting friction, now reached with about 40 grams pull instead of 20, occurred at about the same total elastic yield. But it has to be confessed that it was found impossible to obtain conclusive results both as regards the elastic modulus and (to a less extent) as regards the position of the yield-point or of limiting friction. The surfaces, as used, may be described as reasonably clean; they gave an ordinary coefficient of friction 0·25. They were not in the condition used, for example by Hardy[*] (which might perhaps be described as unreasonably clean) when a coefficient of limiting friction for steel on steel as high as 0·74 was obtained.

Feeling that the inconsistencies in the observations were in large measure due to a varying distribution of the friction grip and to varying cleanness of surface, it was decided to try further experiments using glass surfaces. By examining the layer between the surfaces under monochromatic (sodium) light and under white light, it was thought that the interference bands and colours seen should at least indicate the nature of the distribution of the friction grip.

Glass plates of good optical polish were obtained, smaller plates ($2\frac{1}{2}$ cm. square by 0·7 cm. thick) to rest on larger ones; and the friction apparatus illustrated by fig. 1 was modified so that a larger glass plate could be firmly bound to the base of the cast-iron support.

When the upper plate was laid on the lower one and the surfaces examined under monochromatic light, straight parallel equally spaced interference bands were observed, indicating that a wedge of air had been trapped between the plates (see fig. 4). A considerable load (W—W′) could be placed on the top plate without altering the number of bands seen, and the top plate could be slipped all over the lower one without appreciably altering the appearance of the interference bands. If white light were used no bands might be seen (the plates being then everywhere further apart than ·0002 cm.), or more usually coloured fringes[†] would be visible only at the narrow edge A. By manipulation of the top plate the parallel fringes could be replaced by a uniform colour, and by pressing the plates together this colour could be got to change and ultimately to pass through orange, straw, whitish, grey (when the film was of thickness about 10^{-5} cm.) to black; showing that the plates were of good optical polish and that whatever "dirt" had been trapped with the air between the plates could be pressed to very small thickness. The experiments were performed in an ordinary Glasgow atmosphere—not a very clean one—and it should be remembered that glass surfaces are exceptionally hygroscopic.

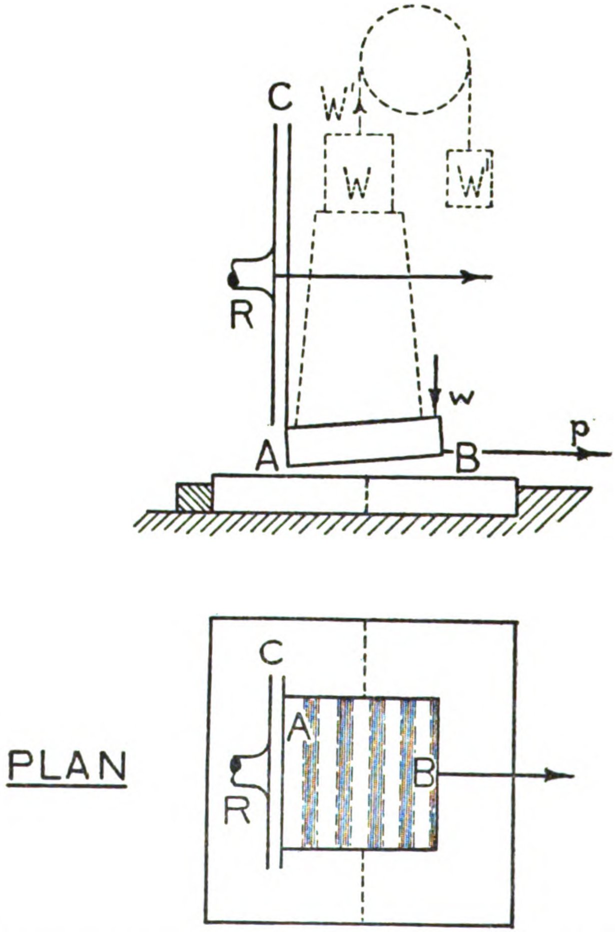
---

[*] 'Dictionary of Physics,' vol. i. p. 576.

[†] For a description of Newton's colours of thin plates and the thickness of film concerned see S. P. Thompson's 'Light Visible and Invisible,' p. 140.

What the nature and distribution of the forces (both normal and tangential) between the two friction plates may be, is a difficult question to answer. The layer between the plates may be of a thickness equal to many wave-lengths of light, or, say, ten or more times the mean free path (10^{-5} cm.) of a gas molecule in the air. The particles in the solid surfaces are thus well beyond the range of direct action on each other—the range of molecular forces being of the order 10^{-6} cm. It is impossible to think of air layers of great thickness bound to the surfaces and (acting like rigid solids)

Fig. 4.



giving support to the upper plate. It might be thought that casual "dirt" in the atmosphere could give a prop-like support which would account for the wedge shape of the trapped layer, and on examining the layer with a microscope (using magnification of only 100) dirt specks could readily be detected; but the fact that the top plate could be moved over the lower one without appreciably altering the appearance of the interference bands is against this supposition. On the other hand, there is no doubt that the surface layers of water and of "grease," referred to by the late Lord Rayleigh in a paper "On the theory of Surface Forces" *, are of fundamental importance in friction problems. Such layers may be quite thick. For example, in an investigation of the heat transmitted through a boiler tube to clean and to oily water, decreases in transmission as great as 20 per cent. were observed, and attributed to oily layers which formed on the surface of the tube. The layers could be readily seen with the naked eye and could be rubbed off the surface of the tube at the conclusion of the experiments; they were estimated as being of thickness of the order one-hundredth of a millimetre.

The approximate permanence, when one plate is moved over the other, of the wedge shape of the trapped layer (illustrated in fig. 4) may be accounted for by regarding the upper plate to be at least partially supported cantilever fashion from the narrow edge A, where the forces in the film will be greatest. That such a cantilever support is possible may be demonstrated by allowing the upper plate to project far beyond the edge of the under one. If the plates at A are close enough to show straw and whitish colour, under white light, the upper plate can be permanently supported with its centre of gravity projecting well beyond the edge of the under plate.

Experiments were also performed using the ultramicrometer to illustrate the distribution of the supporting and tangential forces between two plates. For example, to test for the existence of forces at the wide edge B, of a trapped film, an under plate was cut in two (along the dotted line shown in fig. 4) and an attempt was made to slip out the portion under the wide edge B without permanently altering the capacity of the condenser C. The attempt failed. The half plate could be removed, but there was always a very small permanent change in the capacity of C, even when the half plate was moved very slowly so as to avoid a drag due

---

* 'Collected Papers,' vol. iii. p. 523.

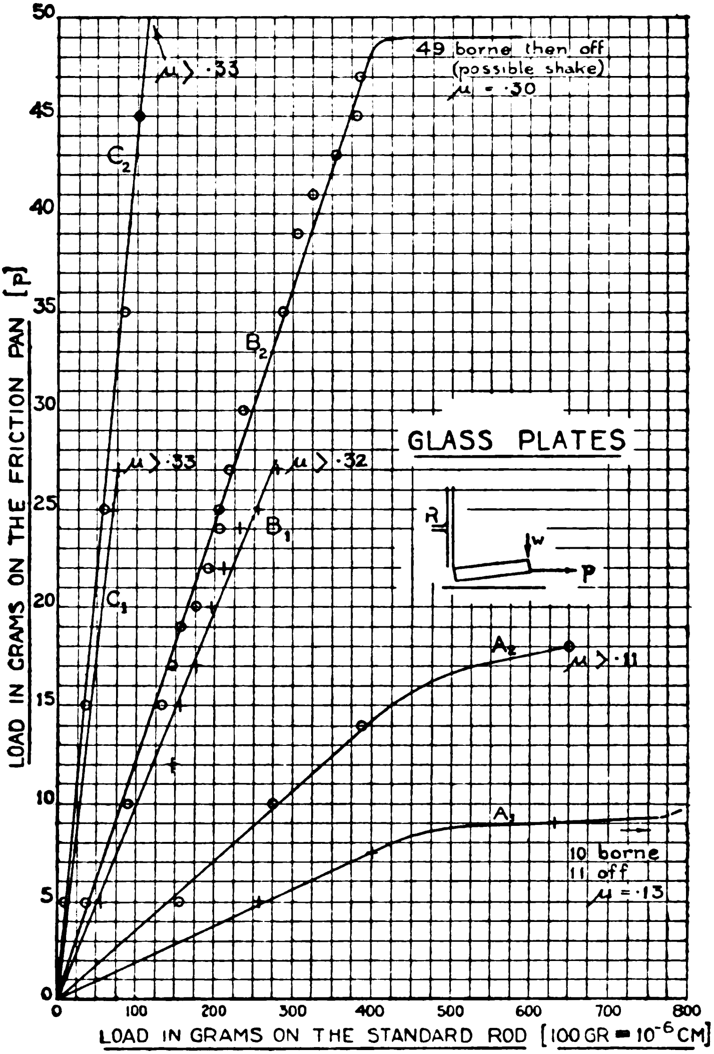
to viscosity in the layer. The small friction force thus shown to exist at B might be due to casual "dirt" or to unavoidable surface layers, but the main forces existed at the narrower edge A.

The effect on the capacity of the condenser C produced by adding a small weight *w* to the top surface of the upper plate was also investigated. By placing *w* above the wide edge B (fig. 4) a much greater elastic change occurred in the capacity of C than by placing *w* above the narrow edge A. An attempt was made to get more consistent results for the magnitude of the tangential strain produced by a pull *p* (see fig. 4), by applying a correction for this tilting action, a correction found by using the principle of moments and the magnitude of the tilt effect produced by *w*; but the attempt failed. For one reason, another complication had to be considered. The main grip at the edge A might be unsymmetrically distributed, so that, when the pull *p* was applied, elastic rotation might occur about a vertical axis somewhere about the letter A shown in the plan, fig. 4. Such a rotation might give rise to either an increase or a decrease in the capacity of the condenser C, depending on the position of the axis of rotation. It was several times observed that, when the friction plates were in very close contact, pull on the upper plate slightly increased the capacity of C instead of decreasing it; the increase in capacity due to the closer approach of the condenser plates at one edge (as the result of rotation) having been greater than the decrease in capacity due to separation at the other edge

When experiments on the elastic range of friction were started, it was thought that by comparing the elastic moduluses got for different materials with the ordinary elastic properties of the materials, some information might be obtained which would throw light on the question why it is we can speak of the coefficient of friction for glass on glass, brass on brass, steel on brass, and so on. The experiments just described show, however, that this idea had to be abandoned. One could never be sure that the distribution of the friction grip was the same in different experiments and the large corrections necessary for tilting and rotation effects would be unknown. Nevertheless the following results obtained with glass, brass, and steel surfaces all of good optical polish, and using two different normal loads, are thought to be worth recording.

Figure 5 shows results obtained with glass surfaces. The surfaces having been well cleaned, the top plate was gently

Fig. 5.



A_1, A_2—No colour with white light: 15 yellow bands with Na light.
$w = 1$ gr. at edge produced same effect as 180 grs. on Rod R.
A_1—Normal reaction 83 grs.; A_2—Normal reaction 166 grs.

B_1, B_2—5 coloured fringes from edge A to rather more than half-way across the plate, then no colour to B, with white light.
B_1—Normal reaction 83 grs.; B_2—Normal reaction 166 grs.

C_1, C_2—Plate pressed on till whitish colour with white light—straw colour all gone
C_1—Normal reaction 83 grs.; C_2—Normal reaction 166 grs.

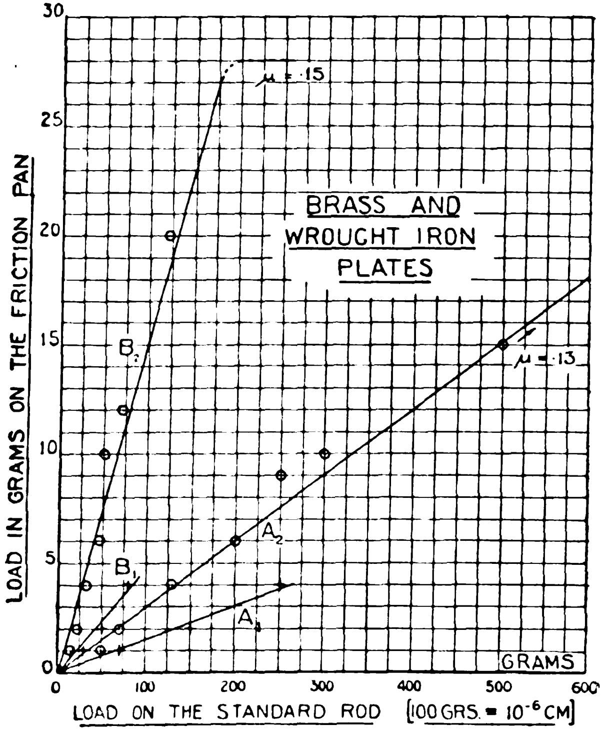
placed on the lower one and adjusted to give a narrow gap between the plates of the condenser C. A weight W, placed on a small stool (see fig. 4), was laid on the top plate—the normal reaction between the surfaces being then 166 grams, or on the average about 26 grams per sq. cm. The layer between the plates was then examined under white light and no coloured bands were seen, so that the plates were everywhere further apart than ·0002 cm. There were 15 bands seen with sodium light (the plates lying as illustrated in fig. 4), so, at the wide edge B, the plates were further apart than ·001 cm. Curves A_1 and A_2 were obtained together, a point on A_1, then a point on A_2. The reduction of the normal reaction (to half value) required for A_1 was obtained with as little disturbance of the friction plates as possible, by applying an upward pull W′ to the load W already placed on the top plate (see fig. 4). The curves indicate that the yield between the plates was not quite elastic right up to limiting friction; and they indicate that there was a yield of more than ·001 cm. before slipping occurred, but of course, due to tilting, the condenser plates would not remain parallel. The effect produced (in the telephones) by placing a little additional load, $w=1$ gram, on the outer edge of the upper plate was the same as that due to applying 180 grams pull to the rod R. The coefficient of limiting friction was 0·13.

Curves B_1, B_2, were obtained with the glass plates in much closer "contact." Five coloured fringes were seen stretching more than half-way across the plates, so the layer between the plates varied in thickness from about ·00006 cm. to about ·00025 cm. The coefficient of friction was about 0·32.

For curves C_1, C_2, the top plate was pressed well on to the under one till the straw colour disappeared, leaving a whitish colour all over, so that the plates were separated by a distance of about ·000015 cm. Due to the breaking of a hook the pull p was not carried up to limiting friction, so the coefficient should probably be much greater than the value ·33 marked on the curves. With very clean surfaces values as high as 0·8, 0·9, greater than unity, had been obtained, but the handling of the plates necessary in these experiments rendered extreme cleanness impossible.

Figure 6 shows similar results obtained using brass and wrought-iron plates of good optical polish. The only method of investigating the character of the layer trapped between the plates was now by means of the little load w. In the case of both brass and of steel it was found that practically the same slight tilting effect was produced by applying *w* anywhere round the edge of the top plate, and no tilting effect was observed when *w* was placed near the centre. This indicates that the surfaces in "contact" were slightly convex, so probably the under plates had been slightly buckled by the application of the strap which bound them to the massive cast-iron support.

Fig. 6.



A₁, A₂—Wrought iron plates.
A₁—Normal reaction 95 grs.
A₂—Normal reaction 176 grs.

B₁, B₂—Brass plates.
B₁—Normal reaction 99 grs.
B₂—Normal reaction 181 grs.

The work described was carried out in the Natural Philosophy Department of the Royal Technical College, Glasgow, and the author desires to express his indebtedness to Messrs. Barr & Stroud Ltd. for kindly supplying the optically polished specimens, and to Professor James Muir, D.Sc., M.A., at whose suggestion the work was undertaken, for assistance rendered during the progress of the research.

Summary.

1. Reference is made to a paper on "Molecular Contact" by James S. Stevens, where it is shown, by an interferometer method, that in an ordinary experiment for finding coefficients of friction, elastic strains are produced before slipping occurs, of magnitudes one or two tenths of a wavelength of sodium light.

2. Apparatus is described for measuring this elastic range of friction by using Whiddington's oscillating-valve ultramicrometer method so that displacements of 10^{-7} cm. could be detected. Results are given for steel resting on cast iron, and an elastic range and "yield-point" for friction are clearly shown. The effect produced by doubling the normal load was tested. It was found that the elastic modulus for friction was thereby about doubled.

3. Inconsistencies in the observations led to experiments being performed with glass surfaces. The layer trapped between the plates could then be examined under monochromatic and under white light. The interference bands seen gave the shape and thickness of the trapped layer and indicated the distribution of the friction grip. This was also investigated by the ultramicrometer, *elastic* tilting and rotation effects, produced by small forces, being measured.

4. Curves are given showing the elastic range and yield-point of friction with glass plates (i.) separated by a trapped layer greater than ·001 cm. thick at the wide edge, (ii.) with a wedge layer ·00006 cm. to ·00025 cm., (iii.) with the plates pressed close together (about ·000015 cm. apart). In each case the effect of doubling the normal load was observed. Similar curves are shown for brass and wrought-iron plates.

LXXIV. *Latent Heats of Vaporization of Ethyl and Methyl Chlorides.* *By* G. W. C. Yates, *B.Sc.**

Method.

THE method used was one of electrical heating and consisted in measuring the amount of heat communicated to the calorimeter containing the liquid under investigation by the heating coil (Q) and equating this to: the heat lost by the evaporation of a determined weight of the liquid, the heat lost by emission (R), and the heat used in raising the temperature of the calorimeter during the experiment ($W\theta$). That is,

$$Q = ML + R + W\theta, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where W is the water equivalent of the calorimeter and contents, θ the rise in temperature from the beginning to the end of the experiment, M the mass of liquid evaporated, and L the latent heat of the liquid.

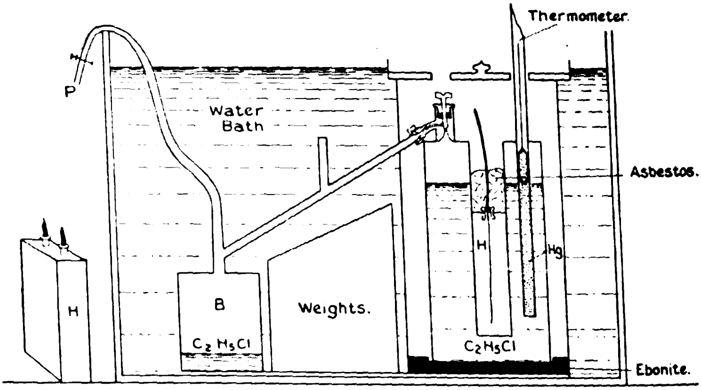
Description of apparatus used for Ethyl Chloride.

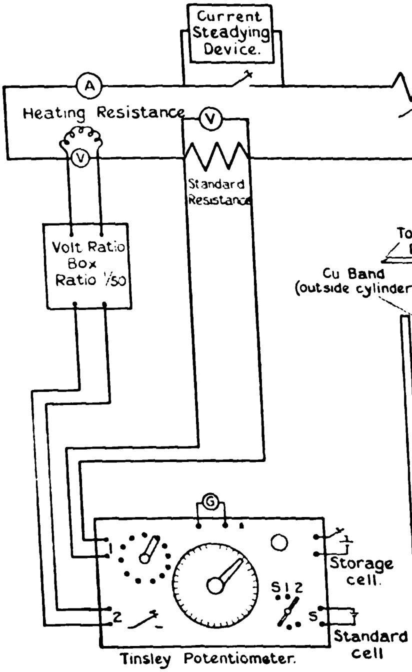
The copper calorimeter was entirely closed except for a cone tap, as shown in fig. 1. The temperature was recorded by a thermometer placed in a thick closed copper tube (communicating only with the exterior) filled with mercury, which ran most of the way down the inside of the calorimeter. The electrical heater (H) was placed in a rectangular prismatic opening in the calorimeter into which it just fitted. Good contact was ensured by the pressure of the liquid and vapour in the calorimeter. This arrangement also secured good stirring of the liquid by convection currents. Several types of electrical heater were tried (during the test experiments); the one ultimately used was of the shape shown in fig. 1. It had a resistance of about 50 ohms, and consisted of nickel-chrome wire embedded in allundum cement (an electrical insulator with good conductivity for heat) contained in a copper case. The vessel containing the calorimeter had a small condensing vessel B attached, and stood in a large bath as shown in fig. 1. The temperature of this bath was kept constant, in some cases by filling it with water and intermittently heating electrically so as to keep it at a constant temperature (above air temperature). The bath was stirred by hand. The lid of the vessel containing the calorimeter was of thick copper ($\frac{3}{8}$ in.) to secure it being as nearly as possible at the same temperature as the tank. The evaporated liquid could be condensed if desired in the vessel B. This was not always done, however, as the duration

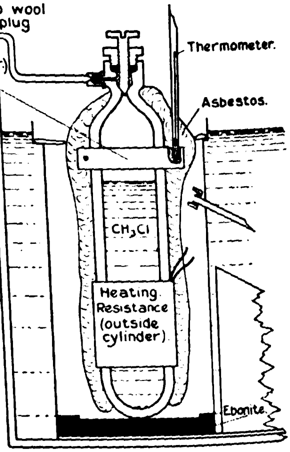
---

* Communicated by Prof. C. H. Lees, D.Sc., F.R.S.

Fig. 1.







To wool plug
Cu Band (outside cylinder)
Thermometer.
Asbestos.
CH_3Cl
Heating Resistance (outside cylinder)
Ebonite.

Fig. 2. Fig. 3.

of the experiment was thereby unduly lengthened. It was therefore allowed to escape at P.

The electrical circuit is shown in fig. 2. The input was determined by measuring the electrical pressures, across the heating resistance, and across a constructed standard resistance R, by means of a Tinsley precision potentiometer. The resistance of this coil R and attached voltmeter was measured by comparison with a standard ohm. The coil R was of No. 12 Eureka wire wound on a wooden frame 18 in. long and of cross-section 6 in. × 4 in. The spacing was very wide so that extremely little change of resistance would result from heating by the current.

Corrections were made for the shunt effect of the voltmeter and volt ratio box on the electrical heater. A current-steadying device was often used to diminish fluctuations in the voltage of the mains. A large coil through which the current passed produced a magnetic field which pulled on an iron bar attached to a pivoted beam which in turn raised a triangular copper electrode in a copper-sulphate resistance cell; an increase in current thus resulted in a simultaneous increase in circuit resistance, so that the increase in current would be much lessened. This device though useful was not entirely satisfactory.

Determination of R.

The heat lost by emission (R) may be determined in two ways.

(1) In which W is first determined.

Temperature time readings of the calorimeter are taken and plotted. A measured amount of heat is put in by the electrical heater (P) and the usual cooling curve drawn. The rise in temperature ϕ which would have obtained if there had been no loss of heat by emission is found.

Then $W\phi=P$, which gives W, the water equivalent. If $-\dot{\theta}$ is the rate of fall of temperature, at the mean temperature of the experiment (or mean rate of fall), $-W\dot{\theta}t$ will be the amount of heat lost by emission (R) during the experiment of duration t. $W\theta$ can also be found as θ is known.

(2) From rate of rise of temperature with various heat supplies.

By measuring the rate of rise $\dot{\theta}_1$ of the calorimeter under a rate of heat supply (p) and the rate of rise $\dot{\theta}_2$ at the same temperature under no heat supply, we can determine the rate at which heat is gained or lost by emission. Considering the calorimeter in the two cases (with and without electrical energy supply) between the temperatures ϕ and $(\phi+\Delta\phi)$, we have

$$p\,\Delta t_1+\mathrm{E}\,\Delta t_1 = \mathrm{W}\Delta\phi$$

$$\text{and} \qquad \mathrm{E}\,\Delta t_2 = \mathrm{W}\Delta\phi,$$

$$\text{or} \qquad p+\mathrm{E} = \mathrm{W}\dot{\theta}_1$$

$$\text{and} \qquad \mathrm{E} = \mathrm{W}\dot{\theta}_2.$$

$$\therefore \qquad p/\mathrm{E} = \mathrm{W}(\dot{\theta}_1-\dot{\theta}_2)/\mathrm{W}\dot{\theta}_2,$$

$$\text{or} \qquad \mathrm{E} = \{\dot{\theta}_2/(\dot{\theta}_1-\dot{\theta}_2)\}\,.\,p, \quad . \quad . \quad . \quad (2)$$

which gives E the rate of gain or loss of heat by emission between the temperatures ϕ and $(\phi+\Delta\phi)$. Then $-\mathrm{E}\,.\,t$ will be the amount of heat lost during the experiment of duration t.

$\mathrm{W}\theta$ can be written as $\mathrm{W}\dot{\theta}_2(\theta/\dot{\theta}_2)=\mathrm{E}(\theta/\dot{\theta}_2)$ and hence determined. E can be found at various temperatures by heating up the calorimeter over some considerable range and allowing it to fall over the same. The appropriate value for the mean temperature of the experiment can then be found.

Test Experiments.

Experiments to test the method were performed on water and carbon tetrachloride. The input was measured by means of ammeters and voltmeters subsequently standardized. In the later experiments on ethyl chloride a precision potentiometer was used for this purpose for the sake of greater accuracy. These experiments gave results in agreement to within ½ to 1 per cent. (accuracy of the meters) of the accepted values.

The calorimeter used in these experiments was found to be unsatisfactory for ethyl chloride, so that shown in fig. 1 was substituted; a better jacketing system also replacing that used in these experiments.

Typical Experiments.

I. C_2H_5Cl. Fri. 18/7/24.

From 1.50 P.M. to 2.26 P.M. the calorimeter fell in temperature owing to loss of heat by emission. The electrical heater was then put on and when a steady rate of rise was obtained the tap of the calorimeter was opened by a screwdriver (2.35 P.M.), allowing liquid to evaporate till 3.2 P.M., when the tap was closed. From 2.35 P.M. to 3.2 P.M. the temperature remained fairly steady, the heat supplied by the electrical heater balancing that lost by evaporation and emission. After 3.4 the rate of rise of temperature again became steady. The experiment is taken from 2.34 P.M. to 3.4 P.M. (duration 30 mins.).

The calorimeter is raised $0^\circ{\cdot}75$ C. during the experiments.
Mean temp. of experiment $= 13^\circ{\cdot}8$ C.
Mean rate of fall/min. due to emission $= {\cdot}200^\circ$ C./min. (at $13^\circ{\cdot}8$ C.).
Loss of weight during experiment $= 91{\cdot}84$ gms.

Then $(\dot{\theta}_1 + \dot{\theta}_2)W$ (see p. 819) $= ({\cdot}712 + {\cdot}167)W =$ mean rate of heat supply from 2.30 P.M. to 2.34 P.M.
Hence

$$W = 1523 \times \frac{10^7}{JS} \text{ cals.},$$

where J is the mechanical equivalent of heat and S the resistance of the standard (·9169 ohm).

Heat lost by emission, etc. during experiment

$$= (30 \times \overline{{\cdot}200} + {\cdot}75)W$$

$$= 10270 \times \frac{10^7}{JS} \text{ cals.}$$

Energy used up in evaporating the liquid

$$= (43440 - 10270) \times \frac{10^7}{JS} \text{ cals.}$$

Hence

$$L = \left\{ \left(33170 \times \frac{10^7}{JS}\right) \Big/ 91{\cdot}84 \right\} \text{ cals./gm.}$$

Then, as $S = {\cdot}9169$ ohms, and correcting for shunt effect voltmeter 3,300 ohms and volt ratio box 12,000 ohms, we have

$$L = 92{\cdot}5 \text{ cals. (at } 13{\cdot}8^\circ \text{ C.).}$$

II. C_2H_5Cl. Mon. 1/12/24.

Here the water equivalent was determined by communicating a measured amount of heat to the calorimeter, observing the times and temperatures, and calculating the true rise by drawing the usual cooling curves. The energy used to counterbalance that lost by evaporation was put in for a certain portion only of the duration of the experiment.

This is more satisfactory than the method employed in the last experiment and was used oftener.

The temperature of the calorimeter dropped $0^\circ \cdot 05$ C. during the experiment.

Mean temp. of experiment $= 13^\circ \cdot 2$ C,

Mean rate of fall/min. due to emission $= 0^\circ \cdot 0483$ C./min. (at $13^\circ \cdot 9$ C.).

Loss of weight during experiment $= 23 \cdot 75$ gms.

Duration of experiment $= 28$ mins.

Loss of heat during experiment due to emission $= (28 \times \cdot 0483)\,W = 1 \cdot 352\,W$.

Loss of heat due to emission $-$ heat given out by calorimeter in falling $0^\circ \cdot 05$ C. $= 1 \cdot 302\,W$.

Corrected rise in temp. in subsidiary experiment for estimating water equivalent $= 5^\circ \cdot 05$ C.

Then
$$5 \cdot 05\,W = 6434 \times \frac{10^7}{JS},$$

$$\therefore \quad 1 \cdot 302\,W = 1658 \times \frac{10^7}{JS}.$$

Hence energy used in evaporation
$$= (10254 - 1658) \times \frac{10^7}{JS}$$
$$= (8596) \times 10^7/JS \text{ cals.}$$

Then putting $S = \cdot 9169$ ohm and correcting also for shunt effect of voltmeter and volt ratio box, gives

$$L = 92 \cdot 6 \text{ cals. (at } 13^\circ \cdot 9 \text{ C.).}$$

Modifications of apparatus for Methyl Chloride.

The method used for methyl chloride was the same as for ethyl chloride, but the cylinder was itself used as the calorimeter. The heating coil was wound round the lower portion of the cylinder and consisted of a thin layer of asbestos paper, a layer of resistance wire, with several layers of asbestos paper on top, and was held in position by a copper sheath. The temperature was read by means of a thermometer placed in a copper cup containing mercury, clamped tight to the cylinder by a copper band. The whole cylinder when in use was covered by asbestos lagging to prevent direct loss of heat from the coil by radiation and convection and in order that the thermometer might read the correct temperature more closely. The same containing or jacketing vessel was used as in the case of ethyl chloride. The expansion of the vapour on coming down to atmospheric pressure was arranged to occur at the far end of a long tube attached to the cylinder so that it should have no appreciable cooling effect on the cylinder. (See fig. 3.)

Results.

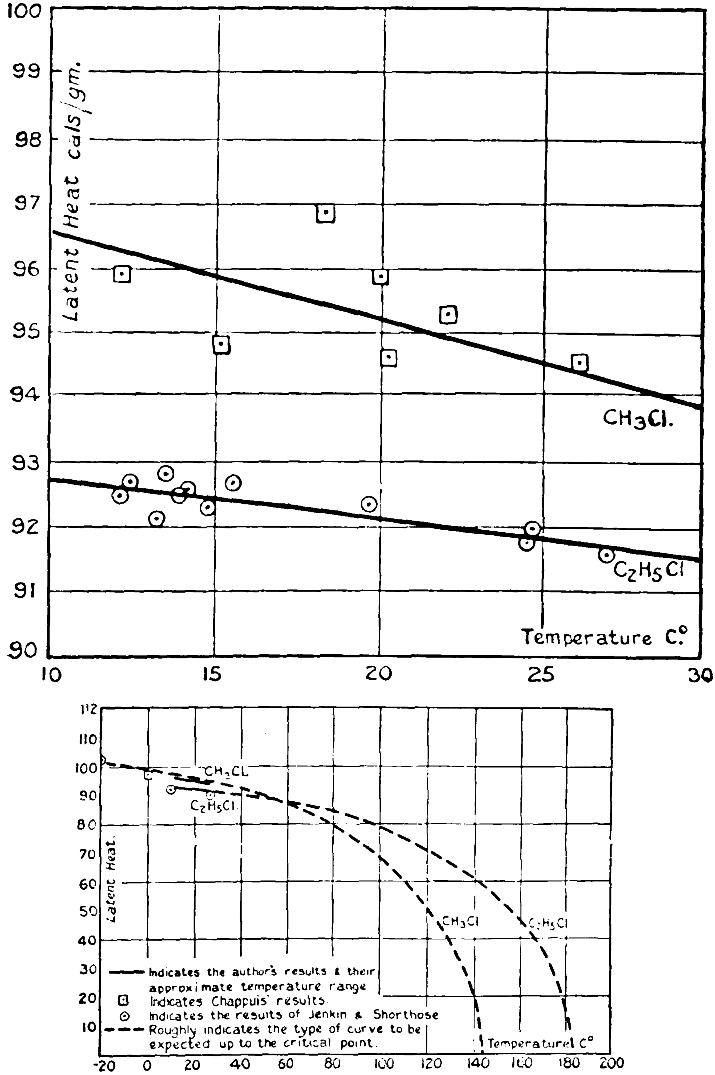
The results are given in the following two tables. They can be represented by

$$C_2H_5Cl \quad L_\theta = (93{\cdot}1 - 0{\cdot}06\,\theta) \text{ cals.}$$

$$CH_3Cl \quad L_\theta = (97{\cdot}7 - 0{\cdot}13\,\theta) \text{ ,,}$$

where L_θ is the latent heat at $\theta°$ C., and J is taken as $4{\cdot}200 \times 10^7$ ergs/calorie, over the range of temperature

Fig. 4.



Results of Experiments on Ethyl Chloride.

Mean temp. of exp.	Wt. of liquid vaporized.	Duration of exp.	$-\dot{\theta}$ in °C./min. (p. 819).	θ° C. (p. 819).	$(R+W\theta)$.	W.S.	$(R+W\theta)\times S$ in joules.	Input Q.S (joules).	$(Q-\overline{R+W\theta})\times S$.	L.
°C.	gms.	mins.								
12·1	19·22	21	0·023	−0·12	0·363 W	1413	513	7454	6941	92·5
12·2	118·27	34	0·177	−2·90	3·12 W	1250	3896	46726	42830	92·7
13·0	21·90	21	−0·013	−1·20	−1·47 W	1215	−1785	6090	7875	92·1
13·8	91·84	30	0·200	0·75	6·75 W	1523	10270	43440	33170	92·5
13·9	23·75	28	0·0483	−0·05	1·302 W	1274	1658	10254	8596	92·6
14·9	14·55	24	0·0159	0·31	0·692 W	1285	889	6132	5243	92·3
15·5	60·20	30	0·0716	−0·30	1·85 W	1004	1858	23660	21802	92·7
19·5	30·30	32	0·023	−0·13	0·606 W	1390	843	11943	11100	92·3
24·2	22·35	16	−0·090	−0·27	−1·71 W	1705	−2916	5095	8011	91·9
23·9	16·75	38	−0·015	−0·95	−1·52 W	1570	−2387	3616	6003	91·7
27·4	49·85	60	0·0172	−1·50	−0·47 W	1307	− 614	17180	17794	91·5

In deducing L from $(Q-\overline{R+W\theta})$ a correction of 1·6 per cent. is made for shunt effects; J is taken as $4{\cdot}190\times10^7$ ergs/calorie, and the standard resistance S has a resistance 0·9169 ohm.

Results of Experiments on Methyl Chloride.

Mean temp. of exp.	Wt. of liquid vaporized.	Duration of exp.	$-\dot{\theta}$ in °C./min. (p. 819).	$\theta°$ C. (p. 819).	$(R+W\theta)$.	W.S.	$(R+W\theta)\times S$ in joules.	Input Q.S (joules).	$(Q-\overline{R+W\theta})\times S$.	L.
°C.	gms.	mins.								
12·2	29·90	30	0·012	−0·50	−0·14 W	788	−110	11080	11190	95·9
15·0	8·55	40	0·000	0·077	0·077 W	809	62	3227	3165	94·9
18·2	24·00	30	0·020	−0·20	0·40 W	810	324	9397	9073	96·9
20·0	40·70	20	0·000	−0·10	−0·10 W	865	−86	15010	15096	94·9
20·2	26·80	26	−0·0154	−0·40	−0·80 W	939	−751	9160	9911	94·7
22·0	28·90	28	0·010	0·12	0·40 W	753	301	11050	10750	95·3
26·0	25·64	35	0·0973	−2·00	1·405 W	806	1133	10610	9477	94·7

In deducing L from $(Q-\overline{R+W\theta})$ a correction of 1·6 per cent. is made for shunt effects; J is taken as $4·190\times10^7$ ergs/calorie, and the resistance of the standard resistance S is given its value 0·9169 ohm.

covered by these experiments (*i. e.* from about 10° C. to about 30° C.). These results together with those of Chappuis and Jenkin & Shorthose are shown graphically in fig. 4. The dotted curves up to the critical points are put in on the assumption that Thiesen's formula, $L_\theta = L_1(c-\theta)^{\frac{1}{3}}$, where L_θ represents the latent heat at θ° C., c the critical temperature, and L_1 a constant, holds for these liquids over this temperature range.

Conclusion.

The following is a list of previous determinations of the latent heat of ethyl chloride (in cals./gm.). The author's values are included for comparison.

Temp.	Regnault (1).	Regnault (2).	Jenkin & Shorthose *.	Yates.
12·5° C.	92·2	92·2	91·5	92·6
21·0° C.	90·7	91·9	89·8	92·0

Regnault determined the total heats †. The column Regnault (1) gives the latent heat calculated from these total heats using Regnault's specific heat values. The column Regnault (2) gives the latent heat calculated from these total heats and from Jenkin & Shorthose's specific heat values.

The following is a list of previous determinations of the latent heat of methyl chloride (in cals./gm.). The author's values are included for comparison.

Temp.	Observer.	Latent Heat.
0° C.	Chappuis ‡	96·9
−23°·8 C.	Shorthose §	102·45
+20° C.	Yates	95·2

The results of Jenkin & Shorthose were unpublished at the time the present investigations were commenced.

In conclusion, I wish to express my sincere thanks to Prof. Lees for suggesting this work, and for his most valuable advice throughout.

---

* Jenkin & Shorthose, Food Investigation Board (Dept. of Sci. and Indus. Research), Special Report No. 14 (1923).

† Regnault, *Ann. Chim. Phys.* (4) xxiv. pp. 423, 438 (1871).

‡ Chappuis, *Ann. Chim. Phys.* xv. pp. 498–517 (1888).

§ Shorthose, Food Investigation Board (Dept. of Sci. and Indus. Research), Special Report No. 19 (1923).

LXXV. *On the Parallel-Plate Condenser, and other Two-Dimensional Fields Specified by Elliptic Functions.* By W. B. Morton, *M.A., Queen's University, Belfast* *.

THIS note is a commentary on certain paragraphs in Sir J. J. Thomson's book, 'Recent Researches in Electricity and Magnetism,' published in 1893. The third chapter of that work is devoted to the discussion of a number of cases of the application of conjugate functions to electrostatics, first by use of Schwarz's transformation, and then by the indirect method in which assumed functional relations between $w=u+iv$ and $z=x+iy$ are interpreted in terms of electric fields. The cases

$$z = sn\,w,\quad cn\,w,\quad sn^{\frac{1}{n}}w,\quad cn^{\frac{1}{n}}w,\quad \log sn\,w,\quad \log cn\,w,$$

are discussed in detail, and expressions are found for capacities and distributions of charge. At the end of the chapter the relation $z=Zw$ where Z is Jacobi's function defined by $E\,am\,u - Eu/K$, is given to represent the case of two equal parallel strips forming the simplest kind of condenser. This is not developed further, owing to the want of tables of the function involved.

I have made drawings of all these fields, and in the last case I have supplied a detailed discussion on the lines of those given in the book for the other fields.

The calculations, from which the families of curves $u=$const. and $v=$const. were plotted, were straightforward and not laborious. The interval from 0 to K or 0 to K′ is divided into ten equal steps in each family, so that there are equal differences of potential between level surfaces and equal charges between the ends of lines of force. The modular angle is 30°, except in the last case, where it is 60°. It will be noticed that the interchange of the meanings of *uv* gives a different arrangement of conductors in the *sn* cases, but not in the *cn* cases. The former fact apparently was not noticed by Sir J. J. Thomson; he used *dn* to obtain the alternative case of *sn*. The functions *sn* and *dn* give identical diagrams.

---

* Communicated by the Author.

The Parallel-Plate Condenser.

The equation $z=Zw$ when developed gives

$$x=Zu+k^2sn\,u\,cn\,u\,dn\,u\,sn^2v/(cn^2v+k^2sn^2u\,sn^2v)$$

$$y=-(Zv+\pi v/2KK')+dn^2u\,sn\,v\,cn\,v\,dn\,v/(cn^2v+k^2sn^2u\,sn^2v).$$

The elliptic functions of the quantity u are taken with modulus $k=\sin\alpha$, those of v with the complementary modulus $k'=\cos\alpha$. The origin of (xy) is at the centre of one of the plates, and the range u from 0 to K, v from 0 to K$'$ covers a quarter of the field. For when $v=0$ we have $x=Zu$, $y=0$; and when $v=K'$, $x=Zu+cn\,u\,dn\,u/sn\,u$, $y=-\pi/2K$. The function Zu vanishes for $u=0$ and $u=K$, and has a maximum for a certain value, u_1 say, determined by the equation $dn^2u_1=E/K$. Therefore the equipotential $v=0$ consists of the two faces of a strip of breadth $2Zu_1$, with centre at the origin. The parallel line $v=K'$ extends from the axis of y to infinity, and is the positive half of the line of symmetry midway between the two plates. Repeating the quarter-plane so obtained, we have the field of the condenser, the distance of the plates being π/K, breadth of a plate

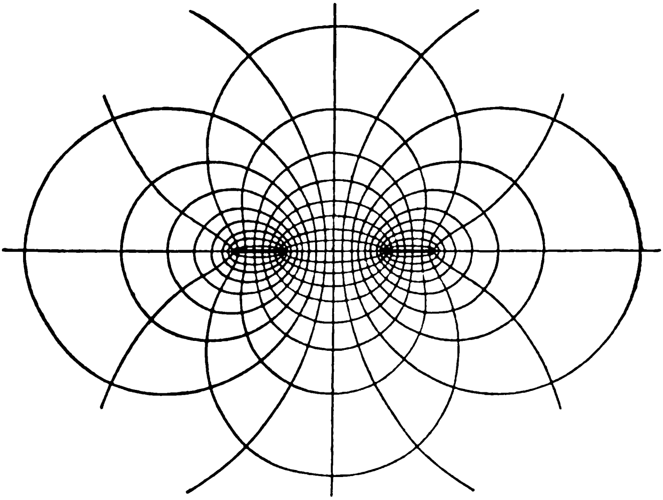
$$2Zu_1=2Z\{dn^{-1}\sqrt{(E/K)}\},$$

charge per unit length on either strip $K/2\pi$, difference of potential between the strips $2K'$.

The capacity per unit length is thus $K/4\pi K'$. If calculated by the elementary formula, which holds when the plates are very close together, the value would be $K.\,Zu_1/2\pi^2$. The ratio of the actual capacity to this, $\pi/2K'.\,Zu_1$, may be called the "capacity-factor," while the ratio of spacing to breadth of plate $\pi/2K.\,Zu_1$ may be taken to specify the shape of the condenser. This ratio approaches zero as the modulus k approaches unity, for the maximum value of the function Z approaches one, while K becomes infinite in a logarithmic manner. The slowness with which K increases limits rather severely the application of the formulæ to practical cases; even when the modular angle is 89°, the ratio of distance to breadth is still ·459. The capacity-factor is plotted against the shape-constant on fig. 8, and the values of the modular angle are marked on the graph. The relation is almost linear in the range of the calculations, but the curve swerves round to touch the vertical axis at the limiting value unity. For $Zu_1=Eamu_1-Eu_1/K$, which approaches $(1-u_1/K)$, so the capacity-factor approaches

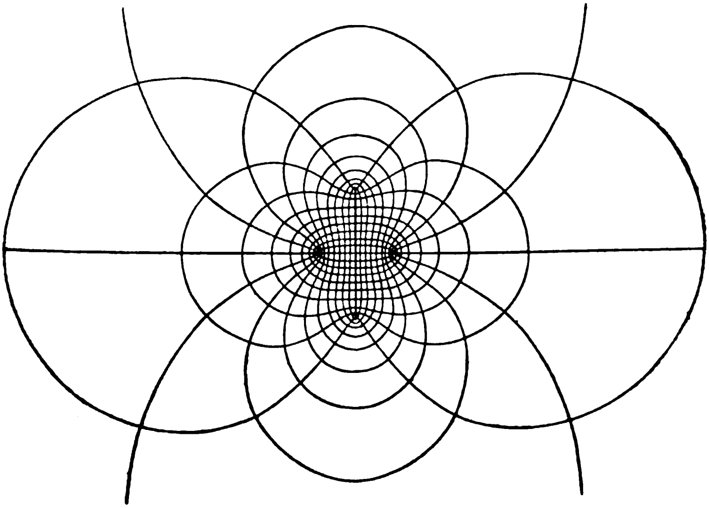
$(1+u_1/\mathrm{K})$, while the shape constant approaches $\pi/2\mathrm{K}$, and (capacity-factor $-$ 1) / (shape-constant) approaches $2u_1/\pi$. As k becomes equal to unity u_1 and K become infinite while the ratio u_1/K approaches zero.

Fig. 1.



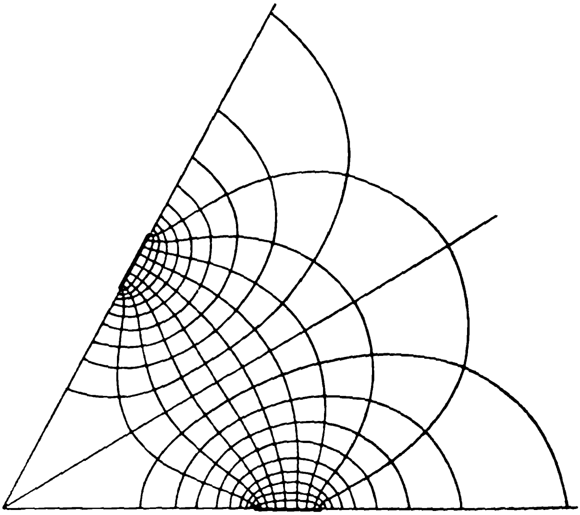
$z = sn\,w$ and $z = dn\,w$.

Fig. 2.



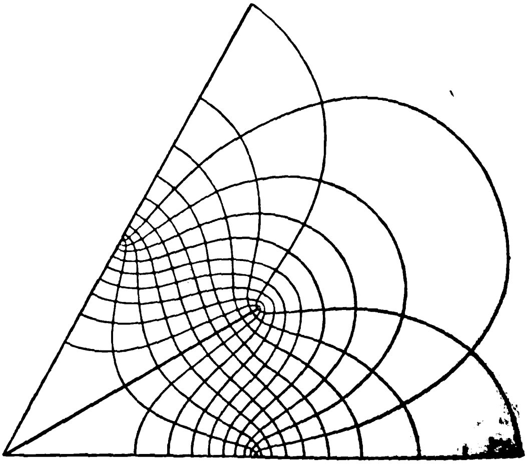
$z = cn\,w$.

Fig. 3.



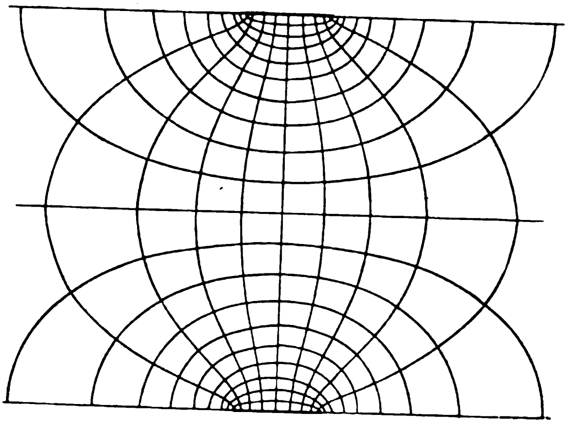
$z = sn^{\frac{1}{3}} w.$

Fig. 4.



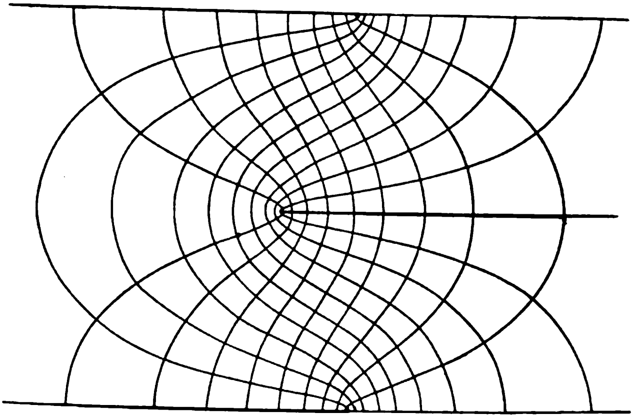
$z = cn^{\frac{1}{3}} w.$

Fig. 5.



$z = \log sn\, w$

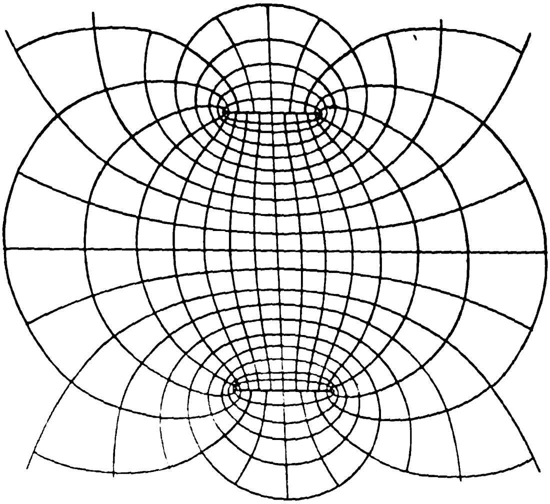
Fig. 6.



$z = \log cn\, w$.

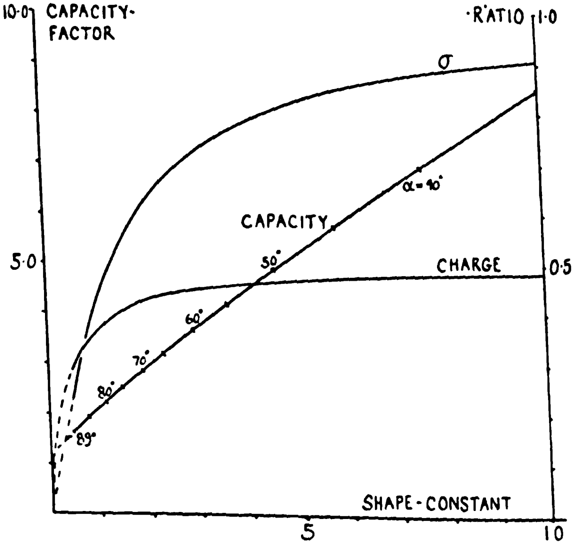
The other curves on fig. 8 show the variation, as the plates are drawn apart, of (1) the fraction of the whole charge on a plate which resides on the outer surface, and (2) the ratio of the surface-density at the centre of the plate on the outer side to that at the opposite point on the inner

Fig. 7.



$z = Zw$.

Fig. 8.



side. These are plotted on ten times the vertical scale of the other curve, the values being marked at the right-hand side of the diagram.

(1) The outer charge is to the whole charge as u_1 is to K. It follows that this curve, close to the origin, is a magnified copy of the graph for capacity-factor near the value unity. So for plates close together we have the result that the fractional increase of capacity, due to the curvature of the lines of force, is equal to the proportion of charge on the outside of the plates.

(2) We have
$$4\pi\sigma = du/dx = du/dZu$$
$$= 1/(dn^2u - E/K).$$

At the centre on the outer side $u=0$,
,, ,, on the inner side $u=K$.

$$\therefore \quad \sigma \text{ outside}/\sigma \text{ inside} = \{(E/K) - k'^2\}/\{1-(E/K)\}.$$

The value ranges from 1 when $k=0$ to 0 when $k=1$.

This graph comes down to the origin at a finite angle with the horizontal. Near the limit $k=1$ we have

$$(\sigma\text{-ratio})/(\text{shape-constant}) = 2/\pi.$$

LXXVI. *The Stability of a Layer of Fluid heated below.*

By HAROLD JEFFREYS, *M.A.*, *D.Sc.*, *F.R.S.**

IT was shown by the late Lord Rayleigh † in 1916 that a liquid might be in stable equilibrium even if its density increased upwards, provided its viscosity was sufficiently great; and a detailed solution was obtained for the mode of decay or growth of disturbances in certain conditions. The results were in qualitative agreement with the experimental work of Bénard ‡, since repeated and extended by A. R. Low and Brunt §. The boundary conditions assumed by Rayleigh were somewhat artificial, and on account of the general interest of the question and the practical importance of some of its applications it is desirable to extend the work to allow for other possibilities.

The method adopted here is based on the principle of "exchange of stabilities." Let us consider for simplicity a system with a finite number of degrees of freedom. If we assume that in a free disturbance from the steady state all the departures vary with the time like $e^{\gamma t}$, where γ is a constant, γ will satisfy an algebraic equation with real coefficients. If then the physical circumstances of the system vary continuously, all the roots of this equation will in general vary continuously. If the system is conservative, and passes from stability to instability, one of the admissible values of γ^2 changes sign by passing through zero. But the vanishing of a root of an algebraic equation implies that the constant term vanishes; and since γ is equivalent to $\partial/\partial t$, the departure from the steady state will satisfy a differential equation involving the independent variable only through its differential coefficients with regard to the time and not explicitly. Thus when the system is on the verge of becoming unstable the equations of motion will have a solution such that the departure from the steady state is different from zero and independent of the time. When instability is attained, the departure involved in this solution will be the one that will grow with the time.

---

* Communicated by the Author.

† Phil. Mag. xxxii. pp. 529–546 (1916).

‡ *Ann. d. Chimie et de Physique*, xxiii. p. 62 (1901).

§ 'Nature,' cxv. pp. 299–301 (1925).

The present system involves viscosity, and therefore is not conservative. It will still be true, however, that γ will involve an equation with real coefficients (possibly of infinite degree). If the rate of increase of temperature upwards is β (which will be taken as negative), it is fairly clear that when the kinematic viscosity ν is great enough any disturbance will die down exponentially with the time, so that every value of γ is real and negative. When ν diminishes algebraically, instability will arise when one of the values of γ first acquires a positive real part. If its imaginary part is also zero, the previous considerations will apply, and a steady departure from the state of equilibrium will be possible. But if as ν diminishes from ∞ to the critical value two of the values of γ coalesce and then become conjugate complexes, they may have finite imaginary parts when their real part vanishes, and the argument will break down. In this case the motion arising when instability develops will be an oscillation with gradually increasing amplitude. The impossibility of such a movement has not been proved in the present paper, but in Lord Rayleigh's discussion it was proved for a special type of boundary conditions, and here I shall only appeal to experiment to confirm that it is not the type of motion that actually does arise when equilibrium breaks down. I shall assume, then, that the uniformly stratified condition of the fluid first becomes unstable when the equations of the problem have a solution different from zero and independent of the time.

2. Let us assume that in the steady state the temperature is βz, the temperature on the floor being taken as zero; here

β is a constant and z the elevation above the floor. Take horizontal coordinates x and y; and let the components of velocity be u, v, and w. Let p be the pressure, V the temperature, ρ the density; and let suffix zero attached to any of them indicate its value at the same place in the undisturbed state, and an accent its departure from the undisturbed value. Let κ, ν, and α be the coefficients of thermometric conductivity, kinematic viscosity, and volume expansion. Then the equations of motion and of heat conduction are

$$\rho\frac{d}{dt}(u, v, w) = -\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)p + \nu\rho\nabla^2(u, v, w) - (0, 0, g\rho), \quad . \; . \; . \quad (1)$$

$$\frac{d\mathrm{V}}{dt} = \kappa\nabla^2\mathrm{V}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

and the equation of continuity is

$$\frac{d\rho}{dt} = -\rho\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right). \quad . \; . \; . \; . \; . \quad (3)$$

The equation of thermal expansion may be taken to be

$$\rho = \rho_c(1-\alpha\mathrm{V}), \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

where ρ_c is the density at temperature zero; the fluid is supposed incompressible.

All these equations reduce to identities in the steady state except the equation of vertical motion, which gives

$$0 = -\frac{\partial p_0}{\partial z} - g\rho_0. \quad . \; . \; . \; . \; . \; . \quad (5)$$

Let us now neglect all squares of departures from the steady state. The d/dt reduces to $\partial/\partial t$ in (1), giving

$$\rho_0\left(\frac{\partial}{\partial t} - \nu\nabla^2\right)(u, v, w) = -\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)p' - (0, 0, g\rho'). \quad . \; . \; . \quad (6)$$

Forming the divergence of both sides of this equation, we may put ρ_c for ρ_0 when multiplied by a small quantity; then

$$\rho_c\left(\frac{\partial}{\partial t} - \nu\nabla^2\right)\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) = -\nabla^2 p' - g\frac{\partial \rho'}{\partial z}. \quad (7)$$

From (3) (4) and (2)

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = -\frac{1}{\rho_c}\frac{d\rho}{dt} = \alpha\frac{d\mathrm{V}}{dt} = \alpha\kappa\nabla^2\mathrm{V}'. \quad . \quad (8)$$

Thus

$$\alpha\kappa\left(\frac{\partial}{\partial t}-\nu\nabla^2\right)\nabla^2 V' = -\frac{1}{\rho_0}\nabla^2 p' + g\alpha\frac{\partial V'}{\partial z}. \quad . \quad (9)$$

Also from (2)

$$\left(\frac{\partial}{\partial t}-\kappa\nabla^2\right)V'+\beta w=0, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

which determines w in terms of V'. Substituting in the equation of vertical motion we have

$$\left(\frac{\partial}{\partial t}-\kappa\nabla^2\right)\left(\frac{\partial}{\partial t}-\nu\nabla^2\right)V' = \frac{\beta}{\rho_0}\frac{\partial p'}{\partial z} - g\alpha\beta V'. \quad (11)$$

Eliminating p' between (9) and (11),

$$\left\{\kappa\alpha\frac{\partial}{\partial z}+\frac{1}{\beta}\left(\frac{\partial}{\partial t}-\kappa\nabla^2\right)\right\}\left(\frac{\partial}{\partial t}-\nu\nabla^2\right)\nabla^2 V'$$

$$= -g\alpha\left(\frac{\partial^2 V'}{\partial x^2}+\frac{\partial^2 V'}{\partial y^2}\right). \quad (12)$$

If the depth is h, the ratio of the term involving $\kappa\alpha$ to that on the right is of order $(\nu\kappa/gh^3)$ which is in general very small. The term in $\kappa\alpha$ will therefore be neglected. (This approximation was made *ab initio* by Rayleigh.) At the same time we shall introduce the condition of marginal stability that $\partial V/\partial t$ is zero. Then (12) simplifies to

$$\nabla^6 V' = -\frac{g\alpha\beta}{\kappa\nu}\left(\frac{\partial^2 V'}{\partial x^2}+\frac{\partial^2 V'}{\partial y^2}\right). \quad . \quad . \quad . \quad (13)$$

Suppose now that V' is proportional to $\sin lx \sin my$, the remaining factor being a function of z only. Put

$$(l^2+m^2)h^2 = a^2, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

so that a is a pure number. Put also

$$z = h\zeta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

so that ζ is zero at the bottom and unity at the top. Then (13) becomes

$$\left(\frac{\partial^2}{\partial\zeta^2}-a^2\right)^3 V' = -\lambda a^2 V', \quad . \quad . \quad . \quad . \quad (16)$$

where

$$\lambda = -\frac{g\alpha\beta h^4}{\kappa\nu}. \quad . \quad \quad . \quad . \quad . \quad (17)$$

3. *The boundary conditions.*

At the upper and lower boundaries some condition must be satisfied by the temperature. If the fluid is in contact with a perfect conductor V' will be zero; if there is no conduction across the boundary $\partial V'/\partial z$ will be zero.

Three conditions must also be satisfied by the velocity components. If there is a rigid boundary, u, v, and w must all vanish. By 2(10) w is proportional to $\nabla^2 V'$. With our hypothesis as to the form of V' the conditions satisfied by u and v reduce to one. Since these components are zero at all points of the boundary, $\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}$ is zero, whence by 2(3) $\partial w/\partial z$ is proportional to w, which is zero. Thus the conditions at a rigid boundary are that $\nabla^2 V'$ and $\frac{\partial}{\partial z}\nabla^2 V'$ are zero.

If in the undisturbed position of a free surface z is constant over it, in the disturbed state w for this value of z will be proportional to $\partial p'/\partial t$, which is zero for marginal stability. Thus $\nabla^2 V'$ is zero. Also $\partial u/\partial z$ and $\partial v/\partial z$ will be zero for all values of x and y over this surface. Hence by differentiating 2(8) with regard to z, we see that $\partial^2 w/\partial z^2$ is equal to $\frac{\partial}{\partial z}\alpha\kappa\nabla^2 V'$. Using the value of w from 2(10) we see that this implies that

$$\frac{\partial^2}{\partial z^2}\nabla^2 V' = \alpha\beta\frac{\partial}{\partial z}\nabla^2 V'.$$

The maximum values of the quantities involved in this equation, if not restricted to be surface values, would be in a ratio comparable with $1:\alpha\beta h$. The latter quantity is the ratio, to the mean density, of the difference between the undisturbed densities at the top and bottom of the fluid, which we have already assumed to be small. Thus our condition will hold only if the quantity on the left, evaluated on the boundary, is only a small fraction of its maximum in the interior of the fluid. Only a trifling error will therefore be introduced if we replace the condition by the assertion that $\frac{\partial^2}{\partial z^2}\nabla^2 V'$ is zero at the boundary. Thus the conditions at a free surface are that $\nabla^2 V'$ and $\frac{\partial^2}{\partial z^2}\nabla^2 V'$ are zero.

Altogether three conditions must be satisfied at both the top and the bottom of the fluid, while the linear equation 2(16) is of the sixth order. Their consistency implies a relation between the numbers a and λ; for a given a the lowest of the values of λ that satisfy this relation (if there are more than one) would give the value of β appropriate to marginal instability if this were the only value of a admitted. Then the value of a that gives the lowest λ so determined will give the first type of disturbance that will grow, and the associated λ will give the value of β for marginal instability.

4. *Rayleigh's problem.*

The conditions adopted by Rayleigh at the boundary are equivalent to the vanishing of V', $\partial^2 V'/\partial z^2$, and $\partial^4 V'/\partial z^4$. His solution therefore corresponds to a fluid with a free surface at both top and bottom, with the temperature maintained constant over both. This is not a natural system, but admits a simple solution, all the conditions being satisfied if V' is proportional to $\sin s\zeta$, where s is a constant, and $\sin s = 0$. Then 2(16) gives

$$(s^2+a^2)^3 = \lambda a^2, \quad \ldots\ldots \quad (1)$$

and the lowest admissible value of λ is given by taking $s=\pi$. Then

$$\lambda = \frac{(\pi^2+a^2)^3}{a^2}. \quad \ldots\ldots \quad (2)$$

We find that λ is least when

$$a = \frac{\pi}{\sqrt{2}} = 2{\cdot}22, \quad \ldots\ldots \quad (3)$$

and then

$$\lambda = \frac{27}{4}\pi^4 = 651. \quad \ldots \quad (4)$$

This result is equivalent to equations (42) and (44) of Rayleigh's paper.

5. *Solution by finite differences.*

The equation 2(16) could be formally solved in terms of exponential functions, but this method would be troublesome, since four of the coefficients of ζ in the indices would be complex, and the boundary conditions would lead to an equation for λ in the form of the vanishing of a determinant of the sixth order with many complex elements. The most convenient method seems to be that of L. F. Richardson, using central differences *. Let us denote by Z the factor of V′ that involves ζ. If the values of the dependent variable are given at equal intervals d of the independent variable, thus,

---

* Mathematical Gazette, July 1925.

$$Z_{-3},\ Z_{-2},\ Z_{-1},\ Z_0,\ Z_1,\ Z_2,\ Z_3,\ \ldots\ldots,$$

the basis of the method is to replace differential coefficients by finite centred differences: thus for example those centred at $\zeta=0$ are

$$Z' = \frac{1}{2d}(Z_1 - Z_{-1}),$$

$$Z'' = \frac{1}{d^2}(Z_1 - 2Z_0 + Z_{-1}),$$

$$Z''' = \frac{1}{2d^3}(Z_2 - 2Z_1 + 2Z_{-1} - Z_{-2}),$$

$$Z^{\text{iv}} = \frac{1}{d^4}(Z_2 - 4Z_1 + 6Z_0 - 4Z_{-1} + Z_{-2}),$$

$$Z^{\text{vi}} = \frac{1}{d^6}(Z_3 - 6Z_2 + 15Z_1 - 20Z_0 + 15Z_{-1} - 6Z_{-2} + Z_{-3}).$$

If the boundary condition at $\zeta=0$ is that Z, Z'', and Z''' vanish, these show that the neighbouring values of Z are of the form

$$Z_2 - 4Z_1,\ -Z_1,\ 0,\ Z_1,\ Z_2,\ \ldots\,.$$

This is the condition for a conducting rigid boundary. For a non-conducting free surface Z', Z'', and Z^{iv} vanish, and we must have the values

$$2Z_0 - Z_2,\ Z_0,\ Z_0,\ Z_0,\ Z_2,\ \ldots\,.$$

The differential equation being of the sixth order, we must substitute for the derivatives from our central-difference formulæ at all points far enough from both ends for the sixth derivative to be formed by this process. The resulting equations should determine λ, and then the approximation may be improved by repeating the calculation for a larger number of intervals and using the principle that the error is of the form $Ad^2 + Bd^4$.

6. *Case of two rigid conducting boundaries.*

The simplest distribution of values of the independent variable to take consists in assuming a value of Z at $\zeta=\frac{1}{2}$, say b, and allowing all others to be determined by the boundary conditions. Then we have $d=\frac{1}{2}$, and

ζ	-1	$-\frac{1}{2}$	0	$\frac{1}{2}$	1	$1\frac{1}{2}$	2
Z	$-4b$	$-b$	0	b	0	$-b$	$-4b$

Forming the difference equation for the middle value, we find

$$\lambda a^2 = 1024+192a^2+24a^4+a^6. \quad . \quad . \quad . \quad (1)$$

To this approximation the minimum value of λ is 540, and occurs when $a=2{\cdot}33$.

Next consider the values of Z at intervals of $\frac{1}{3}$. The solution must be either symmetrical or antisymmetrical with regard to the median plane, and it is clear that the symmetrical solution will be the first to give instability, for it implies that the columns of warm and cold fluid extend throughout the whole depth. With these data only one value of Z needs to be assigned arbitrarily, and we have

ζ	$-\frac{2}{3}$	$-\frac{1}{3}$	0	$\frac{1}{3}$	$\frac{2}{3}$	1	$1\frac{1}{3}$	$1\frac{2}{3}$
Z	$-3b$	$-b$	0	b	b	0	$-b$	$-3b$

The difference equation at either $\frac{1}{3}$ or $\frac{2}{3}$ gives

$$\lambda a^2 = 2187+243a^2+27a^4+a^6, \quad . \quad . \quad . \quad (2)$$

whence the minimum value of λ is 793, and occurs when $a=2{\cdot}69$.

Considering intervals of $\frac{1}{4}$, we now have two values of Z not fixed already, and we take

ζ	$-\frac{1}{2}$	$-\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1	$1\frac{1}{4}$	$1\frac{1}{2}$
Z	$-8b+c$	$-3b$	0	$3b$	$4b+c$	$3b$	0	$-3b$	$-8b+c$

Two independent difference equations must hold at $\frac{1}{4}$ and $\frac{1}{2}$; they lead to two equations homogeneous in b and c. By elimination we have, after some reduction, the quadratic for λ,

$$\begin{aligned}\{10922\tfrac{2}{3}+(512-\lambda)a^2+32a^4+a^6\}\\ \times\{169301\tfrac{1}{3}+(8704-\lambda)a^2+160a^4+a^6\}\\ =(21845\tfrac{1}{3}+1024a^2+16a^4)(60074\tfrac{2}{3}+2048a^2+32a^4). \quad (3)\end{aligned}$$

From the two examples already worked out, assuming that the error in the value of a that makes λ a minimum is proportional to d^2, we see that the true value of a should be nearly 3. Substituting this in (3) and solving for λ, we find that $\lambda=928$. The error of λ is proportional to the square of the small error of a, and therefore is probably unimportant. Thus we have found that when d takes the values $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, the minimum values of λ found are respec-540, 793, and 928. Extrapolating on the hypothesis that the error is of the form Ad^2+Bd^4, we find that the true value of λ is about 1140.

A preliminary solution was constructed by forming the simplest polynomial that would satisfy the boundary conditions and then finding how far it failed to satisfy the differential equation. Other terms were then added to improve the approximation, which was fairly rapid: λ was found to be about 1200. The initial computations were, however, very laborious, and on the whole Richardson's method is much more satisfactory.

7. *Rigid conducting boundary at base: free non-conducting surface at top.*

The method of the last section applies, except that there will no longer be symmetry about the median planes. The first approximation assumes the values

$$\begin{array}{cccccccc} \zeta & -1 & -\frac{1}{2} & 0 & \frac{1}{2} & 1 & 1\frac{1}{2} & 2 \\ Z & -3b & -b & 0 & b & b & b & 2b \end{array}$$

The equation for λ turns out to be

$$\lambda a^2=384+192a^2+12a^4+a^6, \quad . \quad . \quad . \quad (1)$$

and the appropriate values are $a=2{\cdot}08$, $\lambda=256$.

In the second approximation we take

$$\begin{array}{ccccccccc} \zeta= & -\frac{2}{3} & -\frac{1}{3} & 0 & \frac{1}{3} & \frac{2}{3} & 1 & 1\frac{1}{3} & 1\frac{2}{3} \\ Z= & c-4b & -b & 0 & b & c & c & c & 2c-b \end{array}$$

Writing $3f$ for a, and 81μ for λ, we have the equation for μ,

$$\{3+3f^2+3f^4+2(f^6-f^2\mu)\}\{39+5f^2+15f^4-2(f^6-f^2\mu)\}$$
$$=-(5-3f^2-3f^4)(11+9f^2+3f^4) \quad . \quad . \quad (2)$$

Substituting for f^2 in this the values 1·000, 0·885, 0·770 (the intermediate one being chosen because it makes the right side vanish), we find that μ takes the values 5·34, 5·31, 5·39. By interpolation the minimum of μ is 5·30, occurring when $f^2=0{\cdot}911$. Thus $a=2{\cdot}86$ and $\lambda=430$.

From the results obtained for $d=\frac{1}{2}$ and $d=\frac{1}{3}$ we may now extrapolate on the supposition that the error is proportional to d^2. We find that $a=3{\cdot}49$, $\lambda=571$.

As might be expected from the fact that variations of temperature over the upper surface are now possible, instability sets in for a smaller temperature gradient than in either of the cases already considered. But at the same time the absence of the conducting upper surface delays the spread of heat horizontally; it is presumably to this that the higher value of a, corresponding to a shorter critical wave-length, is to be attributed.

8. *Non-conducting rigid boundaries at top and bottom.*

The boundary conditions in this case are that Z′, Z″, and Z‴ vanish at both boundaries. Returning now to the equation 2(16), which takes the form

$$\left(\frac{d^2}{d\zeta^2}-a^2\right)^3 Z = -\lambda a^2 Z,$$

we see that the equation and all the boundary conditions are satisfied by a constant value of Z, provided that

$$\lambda = a^4.$$

Hence instability arises first for a zero, that is, for infinite wave-length, and then for λ very small. In this case therefore there is no possibility of complete stability with the higher temperature below. The movement once initiated cannot be maintained, of course, because there is no means of supplying new energy to the fluid; if the hotter fluid is originally underneath, it will exchange places with that above, and the motion will then gradually die down.

The same would apply if the upper surface was free, so long as it is non-conducting. Conduction over either boundary excludes the possibility of variations of the temperature there, and solutions of the type just considered do not arise then: a conducting boundary is essential to the stability of the arrangement with the hotter fluid below.

9. The conditions of greatest physical interest are probably those discussed in 6 and 7. These are the ordinary cases of liquid heated below, the upper boundary being in the one case a conducting solid, and in the other a non-conducting free surface. I was led to the former by the suggestion of L. H. Adams[*] that viscosity would play an important part in determining the vertical distribution of temperature in the earth's crust just after the solidification of the exterior; for a high viscosity would tend to damp down eddy currents, and the underlying magma might therefore cool at all points

---

[*] J. Wash. Acad. Sci. xiv. pp. 459–472 (1924).

until the viscosity everywhere had reached the critical value needed to prevent such currents, so that the distribution of temperature would become such as to make the viscosity nearly independent of depth. Let us try, then, to estimate the viscosity needed. For a rock magma the thermometric conductivity is probably about 0·01 c.g.s.; α is about 2×10^{-5}. Let us find the value of ν needed to prevent eddy currents in a layer 100 km. thick with a temperature difference of 100° between the top and bottom, so that $\beta=-10^{-5}$. Then from 2(17)

$$\lambda = 2\times10^{23}/\nu,$$

while the critical value of λ is about 1140. Thus ν must be about 2×10^{20} cm.^{2}/sec. to prevent the development of eddy currents that would redistribute the temperature. This is far above any viscosity yet measured, and a fluid with such a viscosity would be experimentally indistinguishable from a solid. For the same value of β the critical value of ν varies as h^4, so that it would be very much reduced if we considered a smaller depth of fluid. If the substance acquires even a small permanent strength at these high viscosities, eddies would be prevented entirely, so that the temperature distribution when currents ceased would be determined by the melting-point. A further tendency to stability would be introduced if there was a concentration of heavier materials towards the bottom. On the whole, then, it seems likely that viscosity would not be the determining factor, though the present discussion does not close the question.

10. The non-conducting free surface above represents the ordinary heating of a fluid from below. There is a familiar domestic instance of complete stability in this case, namely, the burning of porridge when it is not kept stirred. The high viscosity of the material can prevent currents even when the free surface is at ordinary temperatures and the bottom is charring. Taking h equal to 3 cm., βh equal to $-400°$, κ and α equal to the corresponding quantities for water, say 0·0015 and 10^{-3} (both varying notably with temperature), we have

$$\lambda = 10^7/\nu,$$

while the critical value of λ is about 571. Thus stability would be maintained if ν were something like 1700 cm.^{2}/sec. The viscosity of Lyle's Golden Syrup is given by Kaye and Laby (1919) as 1400 c.g s., so that 1700 for porridge at the stage when it burns is not unreasonable. (It is capable of being poured, so that we are dealing with a case of viscous stability and not of solidification.)

Of course the effect of stirring is to promote rapid mixing and thereby to reduce the difference of temperature between the top and the bottom, the supply of heat at the bottom remaining the same. The eddy currents introduced by stirring take the place of those caused purely by heating, so that the heat can be got rid of at a temperature gradient much less than that needed for instability due to heating alone.

LXXVII. *Growth of Eddies in a Viscous Fluid.*

By Prof. H. Levy, *M.A.*, *D.Sc.*, *Imperial College of Science* *.

THE mechanism of eddy production in a viscous fluid is not yet precisely understood, although as an observed phenomenon it is among the most common. Little more can be said to be known about it than that it appears almost invariably to be associated with states of unstable flow and with turbulent motion generally.

The works of Osborne Reynolds and that of a large number of subsequent investigators, including many of those engaged in aerodynamical research, point to the fact that for many conditions of viscous flow there would appear to exist a critical state corresponding to a particular value of the number vl/ν for which the motion passes from one of comparative steadiness and apparent stability to one of instability and possibly turbulent and eddying motion. Both below and above this critical phase, vorticity in the mathematical sense is known to exist in the fluid, but it is generally true that only above the critical position does the spinning or eddying motion which is naturally associated with vorticity make itself apparent to any marked extent. What in fact is an eddy? and if as would appear reasonable it is nothing but a vortex grown to visibility, how does a vortex *grow* in a viscous fluid?

Consider what happens in the neighbourhood of the sharp projecting edge of a body in motion in a fluid. At slow speeds—that is, below the critical value of the appropriate Reynolds' number—a state of affairs closely resembling the classical "discontinuous" motion appears to exist for a short distance behind the body. The surface of "discontinuity," or rather the surface of most rapid velocity gradient, starts off from the projecting edge, for a short distance remains clearly defined, and then becoming sinuous in form loses its identity in the general stream of fluid. At higher values of Reynolds' number the sinuosities increase in magnitude close to the projecting edge, and the discontinuous surface appears to wind itself up at points forming nuclei round which more and more fluid circulates.

---

* Communicated by the Author.

Maturity for the eddy so formed appears to be attained when in the process of its passage down stream its distance from the projecting edge becomes too great for the vorticity there being produced to be drawn within the ambit of the receding eddy, and a new centre of rotation begins to make its appearance. The subsequent history of the eddy already shed appears merely to be one of gradual decay as its energy is absorbed by the viscous action of the fluid.

The breaking up of the surface of discontinuity into distinct eddies is not easily explained by an examination of the analogous process in a perfect fluid. Kelvin has indeed shown that such a surface is unstable, but it does not follow that anything further will occur in that case than a mere drastic change of shape of the surface. The separation up into *discrete* vortices does not appear to be necessarily involved.

Moreover, this vital distinction does exist between the interaction of separate vortices in a perfect fluid and that of eddies in a viscous medium, that whereas in the former a system of vortices during their interplay will always retain their separate identities irrespective of their relative strengths and signs, in the latter case experiment shows that an eddy may change in intensity apparently by directly absorbing any number of others, the system coalescing into one or more distinct eddies, and then gradually decaying.

If the foregoing description is accurate in its general outline, an essential feature is that the interaction between vortices of the same sign in a viscous fluid should be such as to lead towards coalescence particularly in the early stages of formation, that is to say when the motions are slow. This, then, is a problem in viscous fluid that might legitimately be studied on the assumption that the inertia terms in the equation are negligible.

Taking the simple case in which each element of the fluid is rotating in a plane parallel to (xy) about the axis of z, it can easily be shown that, if ψ be the stream function and $r^2=x^2+y^2$, the equation of motion is

$$\frac{1}{\nu}\frac{\partial\psi}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\psi}{\partial r}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

while the pressure equation gives

$$p-p_0=\int_{\infty}^{r}\frac{\rho\Omega^2}{r}dr, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Ω is the tangential velocity at any point. These equations may be established directly from a consideration of the motion of a single element or by direct integration of the usual equations in (xy) coordinates along a radius and round a circle with centre at the origin.

Any solution of (1) will correspond to a maintained or a decaying rotatory motion about the z axis. Any given initial motion of this type established at $t=0$ may be examined for its subsequent history by considering the solutions of (1) of the type

$$\sum_{1}^{\infty}e^{-\lambda_n t}f_n(r),$$

where it is easily seen that $f_n(r)$ is the Bessel Function of order zero of a certain multiple of r. Let us instead seek for solutions which are functions of $r^2/t=\theta$.

Then
$$\frac{\partial}{\partial t}=\frac{\partial}{\partial\theta}\left(-\frac{r^2}{t^2}\right)=-\frac{\theta}{t}\frac{\partial}{\partial\theta},$$

$$r\frac{\partial}{\partial r}=\frac{\partial}{\partial\theta}\left(\frac{2r^2}{t}\right)=2\theta\frac{\partial}{\partial\theta},$$

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)=\frac{4}{r^2}\theta\frac{\partial}{\partial\theta}\left(\theta\frac{\partial}{\partial\theta}\right).$$

Thus(1) becomes

$$-\frac{\theta}{\nu t}\frac{\partial\psi}{\partial\theta}=\frac{4\theta}{r^2}\frac{\partial}{\partial\theta}\left(\theta\frac{\partial\psi}{\partial\theta}\right)$$

or

$$4\frac{d}{d\theta}\left(\theta\frac{d\psi}{d\theta}\right)+\frac{\theta}{\nu}\frac{d\psi}{d\theta}=0,$$

$$\theta\frac{d\psi}{d\theta}e^{\theta 4\nu}=\mathrm{A},$$

Thus

$$\psi=\mathrm{A}\int\frac{d\theta\,.\,e^{-\theta/4\nu}}{\theta}+\mathrm{B}.$$

It follows that

$$\psi = \mathrm{A}\,.\int_0^r \frac{dr(1-e^{-r^2/4\nu t})}{r} = \mathrm{A}\int_0^{\phi} \frac{d\phi(1-e^{-\phi})}{\phi}$$

is a solution of (1) where $\phi = r^2/4\nu t$.

Nature of the Solution.

When $t=+0$, the distribution is that due to a single line vortex of the logarithmic type coincident with the Z axis. As $t \rightarrow +\infty$, $\psi \rightarrow 0$ and $\frac{\partial\psi}{\partial r} \rightarrow 0$, so that the motion represents that of the decay of this logarithmic vortex in a viscous fluid.

The vortex will be initially of the strength K if $\mathrm{A}=\frac{\mathrm{K}}{2\pi}$. For circles and times for which $r^2/4\nu t$ is constant the circulation will be constant and equal to $\mathrm{K}(1-e^{-r^2/4\nu t})$, so that a circle (r_0, t_0) will continue to enclose a constant amount of vorticity if its radius grows at a rate $\frac{r_0^2}{2t_0}.\frac{1}{r}$, or alternatively if the *area increases at a constant rate.*

At all times subsequent to $t=0$ the velocity at the centre is zero, while the angular velocity there is a maximum and dies off as t^{-1}.

The circle of maximum velocity is given by $r^2/4\nu t=\lambda$, where $e^{\lambda}=1+2\lambda$, *i. e.* $\lambda=1{\cdot}257$.

The solution so far obtained satisfies the equations of motion without restriction as regards slow motions. If now we consider the problem initially proposed—that of the interaction of eddies—we may legitimately impose the restriction regarding slowness of motion. In this case, the equations of motion become linear in form, viz.:

$$-\frac{1}{\rho}\frac{\partial p}{\partial x} = \frac{\partial u}{\partial t} - \nu\nabla^2 u,$$

$$-\frac{1}{\rho}\frac{\partial p}{\partial y} = \frac{\partial v}{\partial t} - \nu\nabla^2 v,$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0.$$

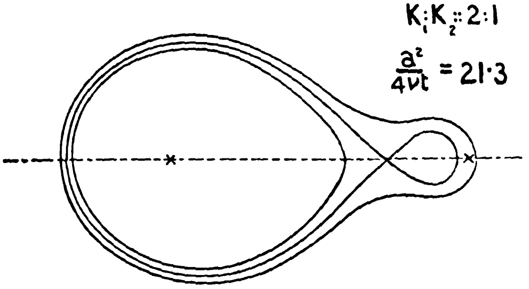
Solutions of the form already found may be superposed, say:

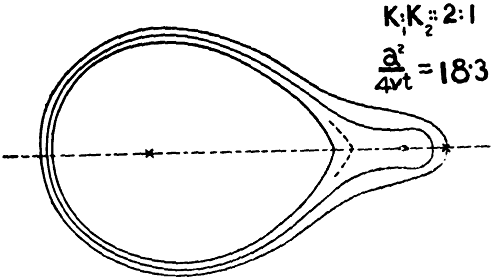
$$\psi_1 = \frac{\mathrm{K}_1}{2\pi}\int_0^{\phi_1} \frac{d\phi_1(1-e^{-\phi_1})}{\phi_1}, \quad \psi^2 = \frac{\mathrm{K}_2}{2\pi}\int_0^{\phi_2} \frac{d\phi_2(1-e^{-\phi_2})}{\phi_2},$$

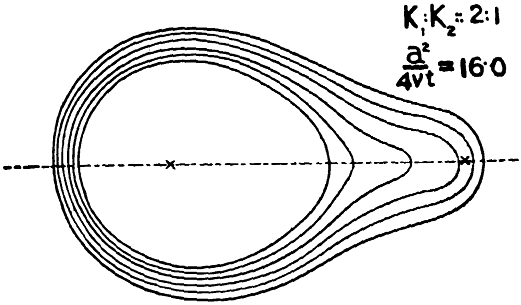
where

$$\phi_1 = \frac{r_1^2}{4\nu t}, \quad \phi_2 = \frac{r_2^2}{4\nu t},$$

and where r_1 and r_2 are the distances of any point from the initial centres of the eddies. The stream function ψ at any point will be $\psi_1+\psi_2$, and the motion will be that arising from the sum of the separate effects of the eddies.

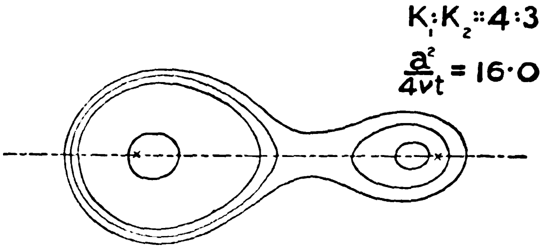


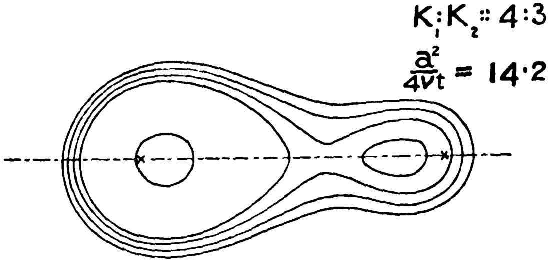


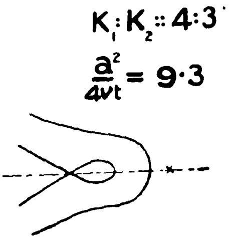


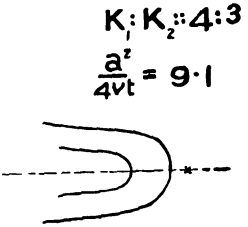
The geometrical shape of the stream lines at any instant will depend on the values assumed by $a^2/4\nu t$ and K_1/K_2, where a is the distance between the eddies at birth and K_1, K_2 are their initial strengths.

In the attached figures the stream lines are drawn for different values of K_1/K_2 (taken positive) and $a^2/4\nu t$. Thus they represent the interaction between two eddies of like but unequal strength created at the same instant. It is clear that with given $a^2/4\nu t$ the stream lines for K_2/K_1 will merely be the reverse of those for K_1/K_2. As t increases, the eddies rotate round each other and the two centres of rotation as long as they remain distinct move towards each other. They do not, however, remain distinct up to coalescence, since for each value of K_1/K_2 there is a









particular time, or more properly a particular value of $a^2/4\nu t$ at which the closed curves round the weaker eddy vanish and for smaller values of $a^2/4\nu t$, that is for subsequent times, the stream lines consist merely of a single system of closed curves. This critical value determines the total life of the weaker eddy as a distinct entity. It is of course a function of K_1/K_2, and could be determined analytically from the expression for ψ if required, instead of graphically as here.

This analysis indicates, then, how eddies grow by absorbing their weaker neighbours while at the same time their combined energies degrade gradually into heat.

Now consider what happens in the neighbourhood of a cylinder past which a fluid is in motion. It is known that in the immediate vicinity of the surface there is a layer of fluid of the order of thickness $10^{-2} \times l$ where l is the length of the body, of exceedingly high velocity gradient ranging from zero velocity at the surface of the body to almost the full value V on the outer surface of this layer. Let us suppose that along the outer layer a series of elementary vortices are created spaced on the average a distance a apart. The strength from vortex to vortex will vary, according to its position along the surface and to the speed of the fluid.

Neighbouring vortices interacting as they pass along the surface will coalesce, and if the time taken for the vortices to pass from nose to tail of the body is large compared with the time of total coalescence, two large eddies, one on the upper surface and one on the lower, of opposite signs will be discharged at the tail. Meanwhile the process of absorption will have recommenced near the nose, a new eddy will grow like a snowball and be finally discharged: thus a periodic generation of eddies will result.

Now let S be the length of surface from the stagnation point at the nose, to the point of departure of the final eddy. If V is the velocity of the fluid at infinity the velocity of the fluid on the outer surface of the boundary layer will range from zero at the nose to approximately V at the point of departure, and the time taken by the accumulated eddy to pass over this distance is approximately 2S/V. If, however, the velocity of the fluid be increased this time will be diminished, so that the interval during which eddy coalescence will occur along the surface of the body will diminish. This suggests at once that if the present standpoint is accurate there may exist a critical speed above which periodicity in eddy formation should disappear. It is not difficult to estimate the order of Vl/ν at which this ought to occur. The criterion will be found by recognizing that if the time of passage of a particle of fluid from stagnation point to leaving point is less than the time required to effect concentration between a pair of vortices, no very definite periodicity will be evident, since the vorticity will not make itself evident as eddying.

We will assume that the results of the earlier analysis may be approximately applied, that for example if $K_1/K_2=2$,

$$\frac{a^2}{4\nu t} \doteq 20.$$

Suppose that the ratio of strengths between two neighbouring vortices is as great as this, then $\frac{a^2}{4\nu t} \doteq 20$. The distance between two vortices may reasonably be taken to be of the order of thickness of the boundary layer so that $\frac{a}{l} \doteq 10^{-2}$, where l is the length of the body; then the time taken for coalescence is at least

$$\frac{a^2}{80\nu} = \frac{10^{-4} l^2}{80\nu}.$$

The critical state will occur when this quantity is of the same order of magnitude as $2S/V$,

$$\frac{10^{-4} l^2}{80\nu} = \frac{2S}{V} = \frac{l}{V},$$

assuming that the eddies leave the surface approximately halfway to the tail.

Thus

$$\frac{Vl}{\nu} = 8 . 10^5.$$

This of course is possibly much beyond the region of periodicity, since for smaller values of Vl/ν the time occupied by the vortices in transit will be sufficient to allow only a few to coalesce, and it is to be noticed that since we have assumed a/l to be of the order of 10^{-2} the number of elementary vortices must be of the order of a hundred.

In a recent paper * Relf and Simmons have determined the variation of periodicity in eddy formation for circular wires over a wide range of values of Vl/ν. For values of Vl/ν up to 10^5 they find distinct periodicities, but beyond that range nothing definite could be observed. The present investigation is in conformity with these results, and suggests that the turbulent motion in the rear of the body associated at lower speeds with the discharge of eddies at the edge must have given way to two sharp bands or trails of smaller eddies separating the wake from the rest of the fluid.

---

* Phil. Mag. vol. xlix. (Feb. 1925).

LXXVIII. *Orifice Flow as affected by Viscosity and Capillarity.* *By* H. W. Swift, *M.A.*, *B.Sc.*[*]

Introduction.

APART from its theoretical interest the orifice has important possibilities as a sensitive method for the continuous measurement of liquid flow, the volumetric rate of flow being given by

$$Q = C_d a \sqrt{2gH},$$

where H is the head effective at the orifice, a its area, and C_d the Coefficient of Discharge. The practical problem of the orifice lies in the evaluation of this coefficient for the conditions under which it is required to operate, and the present limited employment of the orifice method is due largely to uncertainty in the prediction of this coefficient and its systematic variations. In the present treatment an attempt is made to examine some of the more important conditions affecting the flow and their effects, and to rationalise the consequent variations in the coefficient of discharge. Particulars of the methods adopted in the experimental work will be found at the end of the paper.

The following symbols are used :—

H, pressure head across orifice;
p, pressure differences across orifice ;
v, velocity (at vena contracta unless otherwise stated);
w, weight of liquid per unit volume ;
ρ, density ;
μ, viscosity ;
ν, kinematic viscosity ;
σ, surface tension ;
f, acceleration.

Other symbols are defined as they occur.

The English gravitational system of units is adopted as convenient in engineering applications, but the usual convention is observed in the definition of kinematic viscosity, $\nu=\frac{\mu}{\rho}=\frac{\mu g}{w}$.

In converting to absolute units the only substitutions necessary are ρg for w and $\frac{p}{\rho g}$ for H.

---

[*] Communicated by the Author.

SUMMARY OF RESULTS.

The main points which it is hoped to demonstrate are as follows.

In a complete account of free orifice discharge as applied to liquids regard must be paid to each of the dimensionless products

$$\xi = \frac{H}{l}, \quad \eta = \frac{\nu}{lv}, \quad \zeta = \frac{\sigma}{wl^2}.$$

Of these, the product η is generally by far the most important in its effects. An increase in the value of η, exemplified by increasing viscosity, will necessarily diminish the coefficient of velocity C_v, but will always tend to increase the coefficient of contraction C_c towards the limit of unity. The coefficient of discharge $C_d = C_vC_c$ will for a re-entrant mouthpiece necessarily increase with increasing viscosity so long as the conditions of free discharge are maintained; for sharp-edged plane orifices the coefficient increases with η up to a certain point and subsequently falls away towards zero; for a rounded orifice it will fall continuously with increasing viscosity. In each case the relation between C_d and η over the useful hydraulic range is practically linear:

$$C_d = C_0 \pm \kappa\eta.$$

The effect of ξ is generally small and for either hydraulic or very viscous flow may usually be neglected. Over the intermediate range it may become important, but it appears rather to modify the relation between C_d and η than to alter its main characteristics.

Capillarity, represented by the product ζ, always tends to reduce the velocity and at the same time to increase the area of the contracted vein. In the re-entrant mouthpiece it has no resultant effect on the coefficient of discharge, but in other circular orifices there always follows a diminution in discharge, which will usually be small and for hydraulic purposes may be allowed for satisfactorily by a correction of the head:

$$h = H - \frac{4\sigma}{wd_c}(C_0 - \tfrac{1}{2}).$$

THE CRITERIA GOVERNING DISCHARGE.

The principle of dimensional homogeneity when applied to orifice flow affords qualitative results which simplify to some extent the laws controlling discharge.

The general theorem due to Riabouchinsky [*] shows that if $Q_1 Q_2 \dots Q_n$ are physical quantities which completely determine a phenomenon, in the specification of which there are k fundamental units, and if the quantities $Q_1 \dots Q_k$ are independent, different in kind and not interderivable, the general relation

$$F(Q_1, Q_2, \dots Q_n) = 0$$

can be simplified into the form :

$$f(\Pi_1, \dots \Pi_{n-k}) = 0,$$

where Π_x is a dimension product of the form :

$$Q_x(Q_1^{\alpha} Q_2^{\beta} \dots Q_k^{\kappa}).$$

It follows that the quantity Q_x may be written :

$$Q_x = P_x \, . \, \phi(\Pi_1, \dots \Pi_{n-k-1}),$$

where P_x is a product of the quantities $Q_1, \dots Q_k$ having the same dimensions as Q_x.

In the application of this theorem, the variables must be chosen with due regard to the physical circumstances, and the only checks we have upon their completeness and correctness are furnished by experimental confirmation of results and by the compatibility of the dimensional relations. In many cases of practical interest it is unlikely that all the relevant quantities will have similar importance, and it is reasonable to assume that if for simplicity certain quantities are omitted, then provided these are judiciously chosen the results will be nearly correct, in the same way that similar well-chosen omissions will not prejudice unduly the results of quantitative analysis. Exclusion from the original list, however, of dimensional quantities (such as the gravitational constant) which are constant under any or all the conditions of experiment leads to logical absurdity, for it would follow that the variation of any single dimensional quantity could have no effect on the phenomenon. A safer procedure is to include all relevant quantities, constant or variable, to proceed with the dimensional considerations and have regard to the constancy of these quantities in the final result.

In the case of free orifice flow (which for present purposes includes flow over notches or weirs of any form) the quantities which appear to affect discharge and completely to determine it are:

---

[*] 'L'Aerophile,' 1907, p. 407. *Cf.* also *Bull. Inst. Aerod. Koutchino*, i.-iv.

$$l_1, l_2, \ldots l_n, \quad \mathrm{H}, v, w, \mu, \sigma, f,$$

and any quantity Q related to the flow as a whole may be written:

$$\mathrm{Q} \equiv \mathrm{F}\,(l_1, l_2, \ldots l_n, \mathrm{H}, v, w, \mu, \sigma, f).$$

A quantity relating to a particular point is likewise defined by

$$\mathrm{Q}' \equiv \mathrm{F}'(x, y, z, l_1, l_2, \ldots l_n, \mathrm{H}, v, w, \mu, \sigma, f).$$

Here H, v, w, μ, σ, f have the significance shown on p. 852, and such quantities as v, f which are variable under the conditions of a single conformation have representative values. The quantities $l_1 \ldots l_n$ are measures of length which determine the geometrical conformation of the efflux arrangements. In comparing for example sharp rectangular orifices of varying proportions, provided the other dimensions be varied in the corresponding ratios, two quantities $l_1\,l_2$ will be necessary and sufficient. Moreover, if the geometrical conformation remains similar, this similarity extending to conditions of approach, roughness, and depth of liquid above orifice, then it may be specified by a single parameter l.

In the statement of variables no assumption is made or implied that any one of the quantities introduced is independent of the other conditions. It is merely assumed that its value is always determinable from some representative value by means of the other variables mentioned. For example, the possibility that the viscosity may vary with the rate of distortion will not vitiate the argument provided that its value at a definite rate of shear be taken as standard. For we have

$$\mathrm{Q} = \mathrm{F}\,(l, \mathrm{H}, v, w, \mu, \sigma, f),$$

and supposing

$$\mu = \phi\,(l, \mathrm{H}, v, w, \mu, f)$$

we can by eliminating μ obtain

$$\mathrm{Q} = \mathrm{F}'(l, \mathrm{H}, v, w, \mu_0, \sigma, f).$$

The acceleration f at corresponding points we may regard as dependent upon the other variables and upon the gravitational constant g:

$$f = \phi_1\,(\mathrm{H}, l, v, w, \mu, \sigma, g).$$

In the same way the velocity may be regarded as dependent upon its value at an agreed point of reference under standard conditions and upon the other variables. Choosing the point of reference at the vena contracta and the standard conditions those given by a 'perfect' liquid, we have :

$$v = \phi_2(\mathrm{H}, l, v_0, w, \mu, \sigma, f).$$

Hence any quantity Q relating to the flow as a whole, by virtue of these two relations, may be written without loss of generality :

$$\mathrm{Q} = \mathrm{F}_0(\mathrm{H}, l, v_0, w, \mu, \sigma, g).$$

But a definite physical relation exists between certain of these quantities :

$$v_0^2 = 2g\mathrm{H}.$$

Hence we may regard either of these quantities as redundant in the general expression, and may write at discretion :

$$\mathrm{Q} = \mathrm{F}_1(\mathrm{H}, l, \mu, w, \sigma, g) = \mathrm{F}_2(v, l, \mu, w, \sigma, g).$$

For the present it will be convenient to consider the former expression, F_1.

By virtue of dimensional equations the six variables in this expression will furnish the three dimensionless products :

$$\xi = \frac{\mathrm{H}}{l}, \quad \eta = \frac{\nu}{l\sqrt{g\mathrm{H}}}, \quad \zeta = \frac{\sigma}{wl^2}.$$

If the head be replaced by the pressure difference and absolute units are adopted, these criteria take the form :

$$\xi = \frac{p}{l\rho g}, \quad \eta = \frac{\nu}{l}\sqrt{\frac{\rho}{p}} \quad \zeta = \frac{\sigma}{\rho g l^2}.$$

Now if Q is the value at the point x, y, z of any quantity scalar or vector related to the motion, and Q_0 is the value of this quantity at the corresponding point x_0, y_0, z_0 under any conditions of flow which may be chosen as a basis of comparison, then we may write

$$\mathrm{Q} = \mathrm{P}f\left(\frac{x}{l}, \frac{y}{l}, \frac{z}{l}, \xi, \eta, \zeta\right),$$

$$\mathrm{Q}_0 = \mathrm{P}_0 f\left(\frac{x_0}{l_0}, \frac{y_0}{l_0}, \frac{z_0}{l_0}, \xi_0, \eta_0, \zeta_0\right),$$

where P is a product of the relevant quantities of the same dimensions as Q. Hence the relations :

$$\xi = \xi_0, \quad \eta = \eta_0, \quad \zeta = \zeta_0$$

provide the necessary and sufficient conditions that $\frac{Q}{Q_0}=\frac{P}{P_0}$ and in particular that any dimensionless quantity $\Pi=\Pi_0$. This result embraces of course the Principle of Dynamical Similarity.

The coefficient of discharge from an orifice is a dimensionless quantity, and it may therefore be expressed in the form:

$$C_d=f\left(\frac{H}{l}, \frac{\nu}{l\sqrt{gH}}, \frac{\sigma}{wl^2}\right)=f(\xi\,\eta\,\zeta).$$

The Ideal Liquid.

In the case of the ideal liquid μ and σ vanish, and the expression for the coefficient of discharge reduces to

$$C_d=f_1(\xi)$$

when a single parameter defines the configuration, and to

$$C_d=f_1\left(\frac{l_2}{l_1}, \frac{l_3}{l_1}, \dots \frac{l_n}{l_1}, \xi\right)$$

in the more general case. The coefficient of discharge for a 'perfect liquid' therefore is independent either of its density or of the gravitational system. There is no dimensional reason, however, why C_d should be constant at all heads for a given geometrical configuration. The question must be decided by other physical considerations or by experiment.

The General Case.

In the general case we have three arguments in the expression for C_d. For strict similarity in a single gravitational system between two motions M_1 M_2 which are controlled by the quantities under present consideration, the following relations must therefore hold:

$$\xi_1=\xi_2, \quad \eta_1=\eta_2, \quad \zeta_1=\zeta_2.$$

These equations require

$$\left(\frac{\nu_1}{\nu_2}\right)^4=\left(\frac{\sigma_1}{\sigma_2}\cdot\frac{w_2}{w_1}\right)^3.$$

This relation between their physical properties is of course in general not satisfied by two different liquids, and it follows that we cannot expect strict similarity between two flows of different liquids, and since the conditions also require

$$\frac{\nu_1}{\nu_2}=\left(\frac{H_1}{H_2}\right)^{3/2}=\left(\frac{l_1}{l_2}\right)^{3/2}$$

it follows that no two different motions with a single liquid can be similar.

The general result, containing as it does three separate arguments, is complicated and unlikely to yield results of practical value as it stands. It indicates the direction in which the laws of flow may most profitably be explored, but it affords no evidence of their form. In order to obtain information on this point, as a basis for the interpretation of experimental results, it will be well to consider separately the effects of the three criteria ξ, η, ζ. In most practical applications of the orifice the effect of these factors is known to be comparatively small, and it will be of some value if even an approximation to the law of discharge can be found to cover this range with sufficient accuracy and indicate under what conditions any or all of the effects may justifiably be neglected.

EFFECT OF SURFACE TENSION.

In all cases of submerged discharge, and in free discharge from large orifices, the effect of capillarity is not likely to be important. It seems reasonable in such cases to neglect it in the general expression, which then reduces to

$$C_d = f(\xi, \eta).$$

The effect of surface tension, however, on the free discharge from small orifices is not negligible. It will in the case of a circular orifice give rise to a pressure difference across the surface of the jet which can be readily calculated at the vena contracta :

$$2\sigma = \Delta p \, . \, d_c = h_s w d_c.$$

The pressure inside the jet at the vena contracta will therefore be increased and the effective head causing discharge reduced by the amount :

$$h_s = \frac{2\sigma}{wd}.$$

In the case of water this correction represents $\frac{\cdot 022}{d_c}$ inches of head, where d_c is measured in inches at the vena contracta, and may therefore be appreciable.

For a perfectly rounded orifice a simple correction of the head will be sufficient, $h = \text{H} - h_s$; but where contraction takes place the effect is not so simple, since, although the pressure at the vena contract is increased, there is no similar appreciation over the annular section $(a - a_s)$ across which the jet contracts. The pressure distribution in the neighbourhood of the orifice will therefore no doubt be modified to some range of values intermediate between those for non-capillary discharge at heads of H and $H-h_s=h$. In this way there will be induced an effect upon the contraction of the jet. The force causing discharge of a perfect liquid may be written :

$$P = wH(a+\Delta a), \text{ where } 0 \leq \Delta a \leq a.$$

Admitting capillarity but not viscosity, the discharge is determined by

$$\frac{w}{g} C_c a v^2 = wHa + wH'\Delta a - wh_s C_c a,$$

where

$$\left\{\begin{array}{lcl} v & = & \text{velocity at vena contracta } = \sqrt{2gh}. \\ h_s & = & \dfrac{2\sigma}{wd_c}. \\ wH'\Delta a & = & \text{resultant deficit of pressure on wall in the plane of the orifice.} \end{array}\right.$$

By hypothesis,

$$wH\,.\,\Delta a \geq wH'\,.\,\Delta a \geq wh\,.\,\Delta a.$$

Hence it follows :

$$C_c = \frac{Ha + H'\Delta a}{2ha + h_s a},$$

where

$$C_0 = \frac{a+\Delta a}{2a}.$$

Writing $H' = H - \lambda h_s$, where $0 \leq \lambda \leq 1$,

we obtain by substitution :

$$C_c = C_0 + \frac{h_s}{2H-h_s}(C_0 - \lambda\,\overline{2C_0-1}),$$

and necessarily :

$$C_c > C_0 \text{ provided C lies between } 0{\cdot}5 \text{ and } 1{\cdot}0.$$

Now the coefficient of velocity $C_v = 1 - \frac{h_s}{2H}$ nearly.

Hence

$$C_d = C_c C_v = C_0 - \frac{\lambda h_s}{H}(C_0 - \tfrac{1}{2}).$$

It follows that surface tension through its effect upon the contracted vein itself will tend to increase the size of the jet, but when $C_0 > \frac{1}{2}$ will necessarily diminish the discharge. This diminution will not be greater than $-\delta C_d = \frac{h_s}{H}(C_0 - \frac{1}{2})$, which for water, taking C_0 as $0{\cdot}65$, gives a maximum value of about $\frac{\cdot 004}{dH}$ when d and H are measured in inches.

Some estimate of the probable value of the effect is obtained by regarding the distribution of pressure in the approach chamber and in the neighbourhood of the orifice as that corresponding to the mean discharging head across the orifice:

$$H' = \frac{H(a - a_c) + (H - h_s)a_c}{a} = H - C_0 h_s.$$

In this case $\lambda = C_0$ and the *fractional* reduction in discharge will be $\frac{h_s}{H}(C_0 - \frac{1}{2})$ nearly, which for hydraulic conditions may be taken as $\frac{\cdot 004}{dH}$. This effect is usually small and may be satisfactorily eliminated by applying a constant correction of $-\frac{\cdot 008}{d}$ inches to the head. It is this correction which has been applied when necessary in the present experimental work.

There will of course be other effects of capillary forces, but they are not easy to separate and evaluate and are likely to be still smaller than that already considered. The general manner in which they will modify the discharge is clear. For a given liquid the effective force will by its nature depend upon the geometry of the system and will be almost independent of the head. The effect of this force on the discharge will therefore vary inversely with the head, and any modification of the coefficient will be of the form $C = C_0 \pm \frac{q}{H}$ where q is of linear dimensions, and to be identified with the particular orifice and liquid.

In the case of the Borda re-entrant mouthpiece it is interesting to observe that surface tension can itself have no effect upon the coefficient of discharge. For the force causing discharge will be

$$wa(H - C_c h_s) = \frac{w}{g} C_c a v^2,$$

and since $C_v = 1 - \frac{h_s}{2H}$ it follows that $C_d = C_c C_v = \frac{1}{2}$, irrespective of capillary effects.

Effect of Variations in Head.

Correct treatment of the effect of variations in head requires some care. The general expression for the coefficient of discharge has reference only to flows in which the artificial geometrical configuration may be defined by a single parameter l. In many discharge arrangements commonly adopted the surface of the liquid in the approach chamber is free to atmospheric pressure. The depth of the liquid above the orifice will therefore vary with the head, so that simple variations in head will necessarily vitiate the conditions of strict similarity. It is found from experiments with a single orifice in a horizontal plane, discharging under constant head but with varying depth of water, that the effect of this change is small but measurable and that discharge increases with the depth. It would therefore appear that although with varying depths the geometrical configuration may not be accurately represented by the single parameter l, results obtained by ignoring such variations in depth are likely to be seriously in error only in exceptional cases. Moreover, dimensional considerations allow us to write in this case:

$$C_d = f\left(\frac{H}{D}, \frac{H}{l}, \eta, \zeta\right),$$

where l refers to the orifice and to the plan dimensions of the approach chamber. In all experiments with surface free to atmosphere, $H = D$. Hence, in spite of the absence of 'artificial similarity,' we may write for such experiments:

$$C_d = f_1(\xi, \eta, \zeta)$$

which function will be theoretically distinct from, but practically similar to, the corresponding expression

$$C_d = f_2(\xi, \eta, \zeta)$$

which defines the discharge when the geometry of approach is the same at all heads and the quantity l is fully representative. The experiments to which reference will shortly be made were nearly all of the free surface type, so that it is the function f_1 which is strictly speaking under discussion.

Variations in the value of the head H will affect both the remaining criteria of flow, ξ and η. Its effect through the latter will be considered in connexion with viscosity; at present attention will be confined to the former, $\xi = \frac{H}{l}$. The necessity for this criterion has not always been admitted. In the study of the flow of liquids in pipes it is found unnecessary in general to introduce the gravitational constant g, and in certain published work on liquid efflux under gravity it has been omitted. The simplification achieved is considerable, for if surface tension can be allowed for or neglected the variables may then be reduced to l, v, μ, w, which afford the single dimensionless product $\frac{\nu}{lv}$, and ξ disappears. The coefficient of discharge is then necessarily of the form $C_d = f\left(\frac{\nu}{lv}\right)$ and a single series of determinations, made for example by varying the head with other conditions fixed, would furnish this function and enable the value of the coefficient for any similar configuration under any conditions to be obtained from a single curve. The question is therefore of some importance.

For a liquid without capillarity or viscosity the coefficient is necessarily of the form $C = f\left(\frac{H}{l}\right)$. Under the hydrodynamical conditions of efflux from the slit orifice and re-entrant mouthpiece it is known that the coefficient has a definite value irrespective of the velocity of discharge and therefore of the head; and there is no physical reason for anticipating departure from this constancy in orifices of other forms. In nature however, apart from 'imperfections' in the liquid, these hydrodynamical assumptions are not strictly tenable.

(*a*) When liquid discharges from an orifice in a vertical plane the head will not be the same for each individual filament, and when measured in the conventional manner from the centroid of the orifice will not accurately represent the mean effective head. Corrections calculated on a rational basis have been proposed * for the rectangular and circular orifice, and these to the first significant order are of the form:

$$C_d = C_0 - \gamma \left(\frac{r}{H}\right)^2,$$

where $\left\{\begin{array}{l} r \text{ is the semi-vertical dimension of the orifice,} \\ H \text{ is the head measured from the centroid of the} \\ \qquad \text{orifice.} \end{array}\right.$

The correction is found in each case to be negligible when the ratio $\frac{r}{H}$ is less than $\frac{1}{4}$; but for large orifices it increases rapidly in importance at low heads, and it is known that under these circumstances the coefficient may actually fall with the head.

(*b*) When an orifice is mounted horizontally the head is conveniently measured from the plane of the orifice, but here the jet is falling during contraction and under ordinary heads

* C. Monteil, *Ann. d. Phys. et Chim.* xxvii. (3) No. 35, p. 139 (1907).

values of the coefficient so deduced are not likely to correspond with those obtained when the orifice is vertical. Experiment shows that this is the case, and also indicates that for sharp-edged orifices up to 1·0 inch in diameter a satisfactory working agreement is obtained if the head is measured from a point about $\frac{d}{6}$ below the plane of the horizontal orifice.

In the case of the ideal liquid, however, it seems likely that the effect of variations in ξ will be small and usually negligible. It does not necessarily follow that this is the case when viscosity and capillarity are admitted. For guidance at this point we shall have recourse to experiment.

Experiments have been made by G. F. Davidson [*] in the hope of establishing η as the sole criterion with submerged rounded orifices. He worked with an oil at different temperatures and found that the value of this argument did not fix the coefficient of discharge. The physical peculiarities of the oil used, however, give rise to some uncertainty as to the correct values of the viscosity to be applied, and the evidence cannot be regarded as conclusive. W. N. Bond [†], working with mixtures of glycerine and water through a sharp-edged drowned orifice, and assuming η as the criterion of flow, obtained results differing considerably from Davidson's and showing variations in themselves up to 3 per cent. from the mean curve. On the other hand, determinations by J. L. Hodgson [‡] of the discharge of air and water through a single orifice in a pipe-line indicate that for what may be termed limpid flow the quantity η, at least up to the limits of experimental accuracy, is a sufficient criterion of the motion. The balance of existing evidence tends therefore to show that the error involved by the omission of the gravitational constant is not large, but it cannot be regarded as established that such an error does not exist, and it was thought well not to dismiss it without confirmation.

Three series of experiments were made bearing upon this point, under the conditions of limpid, fairly viscous and very viscous flow. In each case the discharge was free.

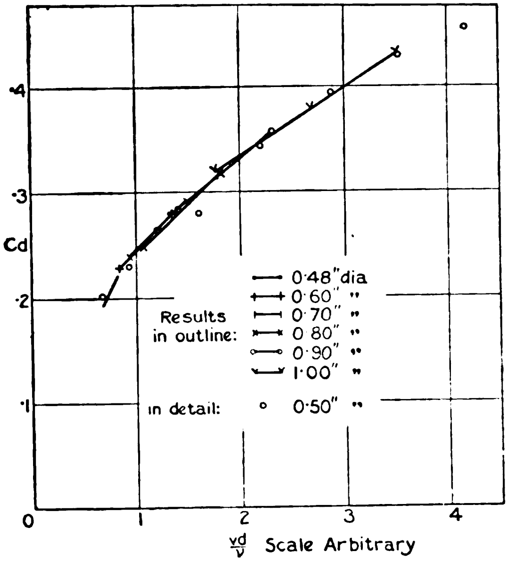
The first series of tests was carried out with an oil of similar properties to that employed by Davidson, having a high viscosity of about $50 . 10^{-3}$ ft.lb.sec. units at 15° C. Variations in the value of the product $\left(\frac{\nu}{lv}\right)$ were obtained by the use of orifices of various diameters from 0·48 to 1·0 inches and by varying the head. The results which are plotted in fig. 1 indicate that for very viscous discharge the single criterion η determines the flow with sufficient accuracy, and that the inclusion of ξ is unnecessary.

---

[*] Proc. Roy. Soc. lxxxix. p. 91 (1913).
[†] Proc. Phys. Soc. xxxiii. p. 225 (1921).
[‡] Proc. Inst. C. E. cciv. p. 192.

In the second series water was used, and a range of values of η was obtained by varying the temperature and head with a given orifice. Two orifices 0·3 and 0·5 inch in diameter were employed and values of the coefficient plotted against η as shown in fig. 2. The results at higher temperatures, possibly owing to the increased difficulty of avoiding turbulence and to inequalities of temperature in the orifice plate and in the liquid, were not so consistent as with cold water. When corrected for attitude and surface tension, however, they show no more serious departure from a single curve than might be due to experimental errors, and it seemed reasonable to conclude that for limpid discharge the criterion ξ could be omitted without serious error.

Fig. 1.



There was, however, in the results some indication of a systematic departure from the single curve, and a third series of tests was therefore made to cover the range of fairly viscous flow. A single orifice 0·1 inch in diameter was employed, and determinations were made with six different liquids varying in viscosity from 2.10^{-3} to $\cdot 024.10^{-3}$ ft.lb.sec. units and under heads between 5 feet

Fig. 2.

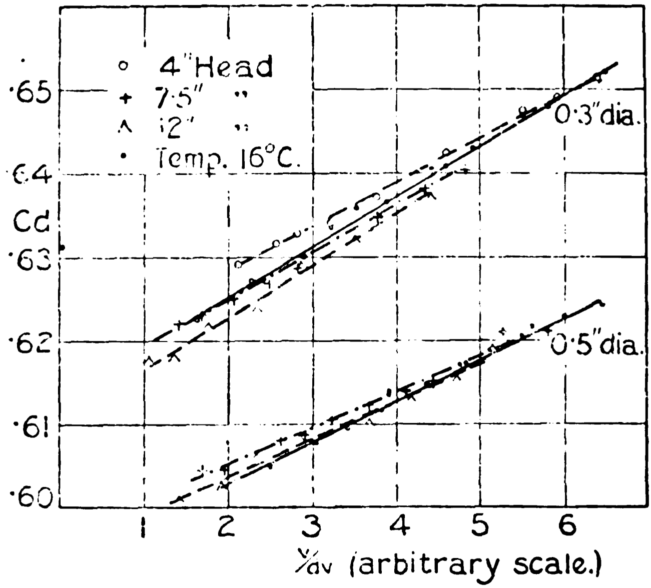
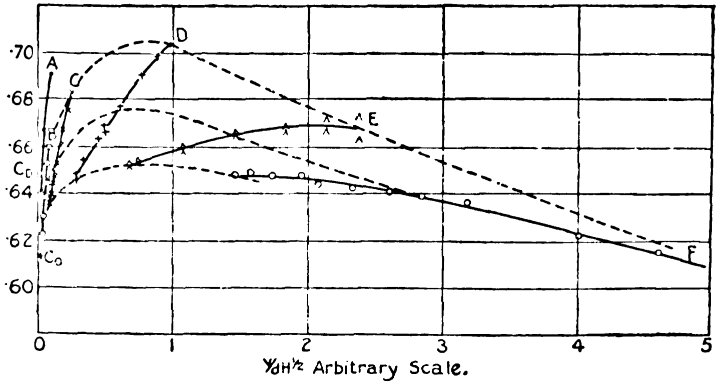


Fig. 3.



and 6 inches. The results are plotted in fig. 3. They show a distinct systematic divergence between the curves obtained with the various liquids, and indicate clearly that over this particular range the discharge is not controlled by the single criterion η. The results have been left uncorrected for capillarity for the sake of clearness. Correction would further accentuate their divergence.

The physical explanation of these results is not altogether clear, but the fact that all the curves may reasonably be considered to converge upon a single point in the limit when $\eta=0$ indicates that the divergence is not to be attributed to any variation in the value of the coefficient for a perfect liquid, and the fact that agreement becomes good again for very viscous flow, where in point of fact there is practically no contraction of the jet, suggests that the effect operates by modifying the contraction in viscous flow, and becomes small with either the viscosity or the contraction. Whatever the nature of the effect, the results furnish definite evidence that not only is it theoretically unwise to omit the gravitational constant in dimensional analysis without examination, but that such omission may lead under certain circumstances to serious errors in application. These results refer only to the case of the free discharge of a liquid into the air, and without further experimental work it would be unsafe to apply them to the conditions of submerged discharge.

So far as the conditions of hydraulic discharge are concerned, however, the divergence is not serious, and a single curve connecting the coefficient with the values of η could be made to cover with good accuracy the range of viscosities over which water is likely to vary in practice. Moreover, the variations indicated in fig. 2 refer to smaller orifices than are normally employed, and agreement will improve as the size of the orifice is increased.

EFFECT OF VISCOSITY.

From considerations already advanced it will be clear that the criterion $\eta=\frac{\nu}{lv}$ * has by far the greatest influence upon the value of the coefficient of discharge, and it is proposed to seek now an approximate relation between the two which shall hold when ξ and ζ are constant or inoperative. The treatment is frankly of a rational nature. The assumptions made are in the main based on known empirical facts, while those specially introduced do not

---

* Writing $C_d=f\left(\frac{H}{l},\frac{\nu}{lv},\frac{\sigma}{wl^2}\right)$.

appear unreasonable and will rely for support upon experimental confirmation of the results.

For simplicity we shall consider in the first instance flows in which H, l, $\frac{\sigma}{w}$ have constant values, so that the kinematic viscosity will be the only independent variable under consideration and the criterion of motion will be $\frac{\nu}{lv}$.

By experimental tests it is found that the total loss of head H_x during approach and discharge is for both water and very viscous liquids proportional to the velocity at the vena contracta. If, therefore, in the criterion $\frac{\nu}{lv}$ the velocity v be defined by its value V at discharge, we may write

$$H_x = \frac{V^2}{2g} \cdot a\eta,$$

where a is a positive number dependent only on the form of the outflow arrangements and the particular values of ξ and ζ. From this it follows at once that the velocity of discharge is given by

$$V^2(1+a\eta) = V_0^2,$$

so that the coefficient of velocity follows the law:

$$C_v = (1+a\eta)^{-\frac{1}{2}},$$

and will of course decrease continuously as the viscosity becomes greater.

Consider now a surface drawn normal to the stream-lines and containing the bounding circle of the orifice. The energy equation at any point on this surface may be written in a common notation:

$$\frac{p}{w} + z = H - \frac{v^2}{2g} - h_x,$$

where v is the velocity at the particular point and h_x the loss of head incurred by the liquid in its movement up to that point. It seems reasonable to assume for descriptive purposes that this loss may be written:

$$h_x = \frac{v^2}{2g} \cdot b\eta,$$

where b is in nature similar to a. Now the curvature of the stream-lines is determined by the pressure gradient across them. At the surface under consideration it follows that

$$\frac{v^2}{g\rho}=\frac{\partial}{\partial n}\left(\frac{p}{w}+z\right)=-(1+b\eta)\frac{\partial}{\partial n}\left(\frac{v^2}{2g}\right).$$

But the velocity v will be less than the corresponding velocity v_0 under non-viscous conditions, and the two are likely to be related in a manner similar to V and V_0:

$$\frac{v^2}{2g}=\frac{v_0^2}{2g}\cdot\frac{1}{1+c\eta}.$$

Hence the curvature will be given by:

$$\frac{v_0^2}{g\rho}=-(1+b\eta)\,\frac{\partial}{\partial n}\left(\frac{v_0^2}{2g}\right),$$

where

$$\frac{v_0^2}{g\rho_0}=\frac{\partial}{\partial n}\left(\frac{v_0^2}{2g}\right),$$

and we have:

$$\frac{\rho}{\rho_0}=\frac{1}{1+b\eta}.$$

The coefficient of contraction C_c is related to the curvature of the stream-lines at discharge by some expression of the form:

$$C_c=\left(1-e\,.\,\frac{\rho}{l}\right)^2.$$

By substitution it follows that

$$1-C_c=\frac{1-C_0}{1+b\eta}-b\eta\left(\frac{1-C_0}{1+b\eta}\right)^2,$$

where C_0 is the theoretical coefficient for the orifice, and since b is necessarily positive this is a continuously decreasing function so long as $C_0<1$.

The value of the coefficient of discharge will be obtained by multiplying C_c by C_v. When the value of η is small we can obtain simple approximations to the coefficients:

$$C_c=C_0+b\eta(1-C_0)(2-C_0),\quad C_v=1-\frac{a\eta}{2}.$$

Whence it follows:

$$C_d=C_0+b\eta(1-C_0)(2-C_0)-\frac{C_0 a\eta}{2}\ \text{nearly}.$$

Whether $C_d \gtrless C_0$ under these circumstances depends upon the comparative values of a and b and is not easily determinable.

In the case of a Borda mouthpiece, for which C_0 is 0·5, the question is settled definitely by the principle of momentum. The force causing discharge will be the unbalanced pressure P over the area of the orifice together with a frictional force F acting along the surface of contact of the re-entrant tube and the liquid. The frictional force will act against the direction of motion of the liquid along this surface, and therefore will actually assist the discharging force P. The principle of momentum then requires:

$$wHA+F = \frac{w}{g}AV_0^2C_dC_v,$$

where

$$wHA = \frac{w}{g}AV_0^2C_0,$$

and it necessarily follows that

$$C_dC_v > C_0$$

and *a fortiori*

$$C_d > C_0.$$

Discharge will therefore increase with increasing viscosity under all conditions so long as the mouthpiece will run free.

In the case of a perfectly rounded orifice the coefficient of contraction is always unity so that the coefficient of discharge will fall continuously. In intermediate cases the instances cited and expressions obtained show that the probability of an initial increase in C_d with η is much greater with low than with high values of the theoretical coefficient C_0.

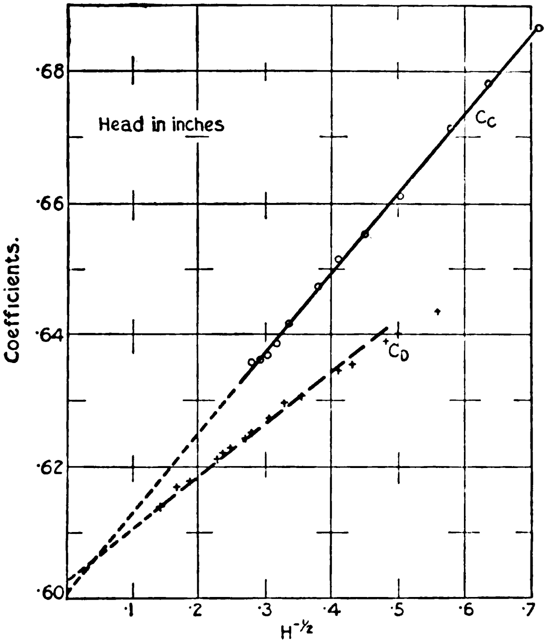
The considerations just advanced have been based on variations in viscosity alone, but the dimensional analysis shows that the results must necessarily hold in the same way for changes in the value of η from any cause which does not affect the values of ξ or ζ. For flows in which this condition holds, or in which these factors are inoperative, we are led to the following conclusions:—

1. An increase in the value of η will always tend to increase the coefficient of contraction from its value C_0 for a perfect liquid towards a maximum of unity. In the case of very viscous liquids we may reasonably expect therefore that contraction will be almost completely suppressed and the discharging jet will have the same dimensions as the orifice. On the other hand, for limpid liquids the expression suggests that over a certain range the coefficient will follow approximately a linear relation:

$$C_c = C_0 + \kappa\eta.$$

Determinations have been made to verify these results. With a very viscous oil discharging from sharp orifices 0·3 and 0·5 inch in diameter no contraction could be detected at heads below about 18 inches. Accurate measurements, however, were difficult to make on account of the adhesive nature of the oil. At greater heads the contraction could be measured, and was found in the case of the 0·3 inch orifice to vary in a manner consistent with the general relation expected to a value of 0·81 under a head of 46 feet.

Fig. 4.

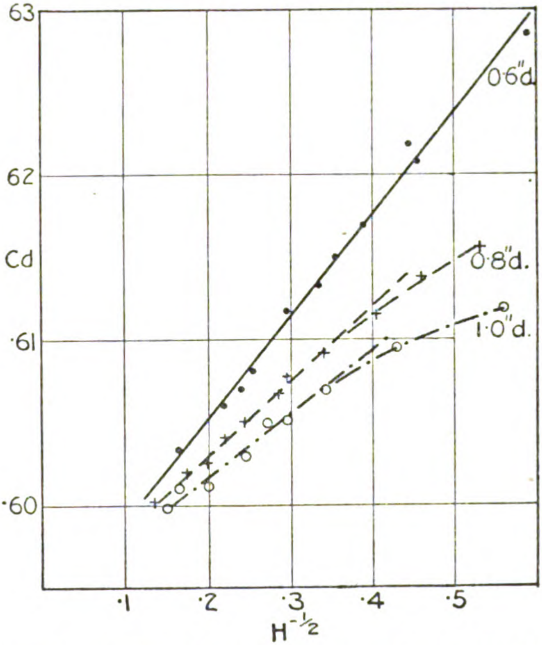


More accurate measurements were made upon the discharging jet of water from an orifice 0·48 inch in diameter, under heads from 2 to 15 inches, The results are plotted in fig. 4, and show the linear relation quite clearly. The linearity is probably helped in this case by the fact that the effect of surface tension on the contraction tends to balance the drooping of the line at low heads, but it is none the less noteworthy. Under the conditions of hydraulic discharge the values of η will normally be still lower, and the linear relation may therefore be safely applied.

2. The coefficient of discharge is dependent upon the value of the coefficient of contraction which continuously

increases and the coefficient of velocity which continuously decreases as η becomes greater. For a sharp orifice the form of the expressions obtained suggests that increments in C_c may at first be greater than corresponding decrements in C_v and the coefficient of discharge will rise to a maximum, beyond which changes in C_v will predominate and it will fall towards zero as a limit. For a rounded orifice changes in C_v will predominate throughout and the value of C_d will fall continuously with increasing η. The earlier part of the curve we may expect in either case to be approximately linear.

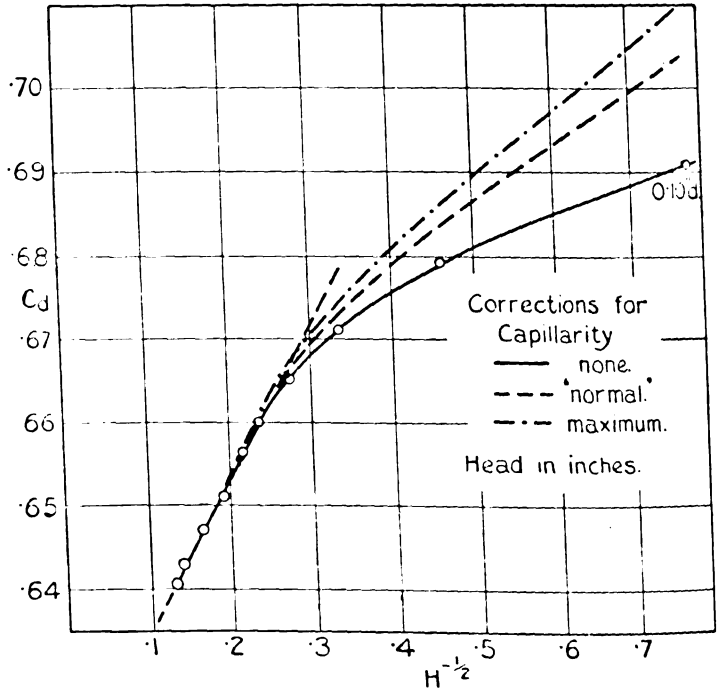
Fig. 5.



A number of experiments were made to verify these conclusions. In these it was assumed that for hydraulic flow and very viscous flow the effect of ξ was unimportant, so that changes in head were admissible in varying the value of η.

(*a*) Determinations of the coefficient of discharge for water from sharp orifices of 0·48 to 1·0 inch in diameter under heads varying from 4 inches to 4 feet showed that the variations were generally in good agreement with the relation expected, corrections having been applied where necessary for capillarity. The collinearity of these results, which are shown in figs. 4 and 5, is at low heads more satisfactory with small than with larger orifices, and with the 1·0 inch orifice the coefficient shows at heads below about 5 inches a distinct tendency to fall. The head in this case is no longer great compared with the diameter of the orifice, and the graduation in head across the section of the orifice begins no doubt to be effective. At the greater heads common in practice collinearity is very marked even without correction for surface tension and shows to better advantage on an open scale. It is noteworthy that these experiments afford no evidence in support of a 'critical head' and a subsequently constant coefficient, and the conditions of viscous flow are easily maintained up to a value of Reynolds' criterion $\frac{vd}{\nu} = 126 \,.\, 10^3$ as compared with the value of 2000 which roughly limits the viscous condition in uniform pipe flow.

Fig. 6.



(*b*) The extent to which the linear relation holds was investigated by determinations of the discharge of water through a smaller orifice about 0·1 inch in diameter. The results (fig. 6) show that, assuming the correction for surface tension is adequate, divergence becomes evident with this orifice at a head of about 10 inches, and since the value of the corresponding head will vary inversely with the square of the diameter it is clearly outside the normal range of hydraulic application. The deviation of the curve from a straight line is in this case to be attributed to the fact that as the Coefficient of Contraction increases towards the limit of unity its rate of increase becomes slower and the Coefficient of Discharge tends to approach its maximum value and subsequent fall.

(*c*) Measurements of the coefficient of discharge under very viscous conditions have already been referred to (fig. 1), and these agree reasonably well with the form expected.

(*d*) The manner in which the C_d, η curve passes over its maximum for a fixed value of the criterion ξ is shown by the dotted lines in fig. 3.

DETAILS OF EXPERIMENTAL METHODS.

a. *Experiments with Water.*

Coefficient of Contraction.

The orifice used was 0·4805 inch in diameter, with edge as sharp as possible bevelled at 45°. The orifice plate was of brass, 8 inches diameter, ⅜ inch thick, and polished. It was mounted in a vertical wall of a tank 24 inches square in plan, and approach was stilled by means of sheets of perforated metal.

Readings of head were made by means of a hook-gauge pointed upwards and a kathetometer. It was found that the hook-gauge was readily sensitive to ·001 inch in still water. The dimensions of the escaping jet were measured by four micrometer depth gauges mounted in a square frame which was adjustable in a vertical plane about an inch from the sharp edge of the orifice. The points of these gauges were sharpened, and contact with the jet was indicated by the formation of ripples on the surface. The measurements were made at times when perfect steadiness could be maintained, and the diameters are considered correct to ·02 mm. During these determinations the jet showed no visible unsteadiness at a distance of four feet from the orifice.

Coefficient of Discharge.

The same orifice was employed in the first instance, and later others of different diameters constructed in a similar way, and screwed flush into a brass orifice plate. The orifice plate was mounted in the wall of the approach chamber and the water stilled as before. Fine adjustment of supply was arranged by means of a bye-pass valve controlling the supply pressure so that the head could be maintained constant during runs.

Heads less than 20 inches were measured by hook-gauge, higher ones by the level in a glass tube connected to the tank. In each case a vernier was used reading to ·01 inch. The jet was steady during runs except in the case of the 0·9 and 1·0 inch orifices under heads of less than 8 inches, when a slight tendency to vortex motion was just discernible occasionally. A swivel pipe below the orifice enabled the tests to be started and stopped with exactitude. The quantity discharged was measured by means of a hook-gauge and vernier mounted on a calibrated rectangular tank, and to ensure consistency the initial and final levels were approximately the same in all determinations.

b. *Experiments with Light Oils.*

The determinations of the coefficient of discharge for light oils plotted in fig. 3 were obtained by timing the fall of level in a calibrated vertical pipe 6 inches in diameter. A control experiment made with water gave results in good agreement with those obtained at constant head. As affording comparative results this method is found simple, expeditious, and reliable, and perfect steadiness is easily maintained. For absolute determinations the more usual method at constant head is preferred. The oils used were of paraffin base and varied from a machine oil to 'paraffin oil' through mixtures of various proportions.

c. *Experiments with Crude Oil.*

The oil was a Mexican crude oil of sp. gr. 0·957 at 15° C., and of a similar nature to that used by Davidson. Its viscosity is high (about $50 \,.\, 10^{-3}$ ft.lb.sec. units at 15° C.) and varies very considerably with the temperature. Moreover, the viscosity is also dependent on the recent history and mechanical treatment of the oil. The normal (minimum) viscosity is only attained after considerable pumping or working, and there is evidence of plasticity until this state is reached. The oil is rich in asphaltic constituents.

Physical homogeneity in the oil during a series of determinations is not easy to secure on account of its high viscosity and low conductivity, which are apt to keep local the quite sensible temperature rise due to continued circulation.

Low Heads.

The same orifices were used as with water, mounted in the same way in a vertical plane. The supply of oil was maintained by means of a ram pump and controlled by a bye-pass valve. Variations in temperature were found to exercise such an important influence that continual readings on a thermometer in the discharge jet were necessary to ensure reliable results. Temperature effects in the results were overcome by running at different temperatures and reducing to standard conditions by interpolation.

Head was measured by hook-gauge in the approach chamber. At low heads it was not possible to maintain a free jet, so that determinations were of no value. The discharge was measured as for water, but owing to the nature of the oil a similar accuracy is not to be expected, and errors up to 1 per cent. are not unlikely.

Greater Heads.

Supply was maintained by pump to a closed approach chamber, and pressure variations due to the fluctuating supply were reduced by a device which had the effect of a large air-vessel. Oil level in the approach chamber was indicated by a mercury gauge.

The head was controlled by means of the air pressure and measured on a mercury gauge connected by a short oil lead to the orifice chamber. It was found that this device followed quite closely the changes in pressure. Control of supply, measurement of discharge, and continual reading of temperature were carried out as at low heads, and in the later work the viscosity was measured during each run by means of a tube fitted to the side of the approach chamber. It was also found more expeditious to weigh the discharge rather than to measure it by hook-gauges.

The author wishes to thank the University of Leeds for facilities in carrying out this experimental work and for supplying most of the apparatus used. His personal thanks are also due to Professor Goodman for his keen interest and encouragement.

Leeds,
December 1925.

LXXIX. *Self-Reversal of the Red Hydrogen Line.*

By R. W. Wood [*].

It is usually assumed that self-reversal of a spectrum line can occur only when a cooler or less powerfully excited layer of the luminous gas lies between the spectroscope and the source of the radiation, as for example when the yellow sodium lines of an arc or bunsen burner are reversed by the mantle of less luminous or non-luminous vapour surrounding the flame. We should not, therefore, expect reversal in the case of an end-on spectrum tube so constructed that no dead-space existed between the discharge and the exit window.

I have, however, repeatedly observed self-reversal of both components of H_α under the above specified conditions.

Experiments were in progress with a view of obtaining, if possible, the resonance radiation of excited hydrogen. A long hydrogen tube, brought to what I have called in previous papers the "black stage" (in which only the Balmer lines are seen when the tube is viewed through a prism, the region between the monochromatic images being quite black), was mounted alongside and close to a second hydrogen tube, feebly excited by comparatively low voltage, and an increased illumination looked for (end-on) when the light of the powerfully excited tube was allowed to enter it. No trace of the phenomenon was found, though Dr. McCurdy, working in our laboratory, has recently observed it in the case of helium, under similar experimental conditions, and it was most beautifully demonstrated to me recently by De Groot in the Philips laboratory at Eindhoven.

Failure to obtain any indication of resonance-radiation under any conditions,—I tried several other arrangements,—made it seem necessary to examine the conditions under which Hydrogen absorbs the light of H_α.

The phenomenon of the reversal of the hydrogen lines in the laboratory has been observed and described many times (Ladenburg and Loria, Hulburt and others). In all of these cases the conditions were not quite the same as those obtaining in the case of resonance radiation. It was necessary to see whether feebly excited, and nearly non-luminous hydrogen, could be made to absorb the two components of H_α emitted by a tube of moderate luminosity or cause their reversal. I accordingly constructed a tube system as shown in fig. 1—A the emitting, B the absorbing tube.

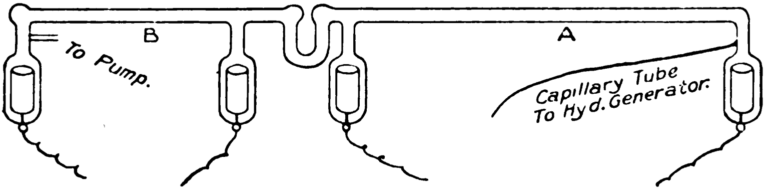
---

[*] Communicated by the Author.

The right-angle bends were blown out paper-thin, so that clear vision through the whole system was possible. The spectroscope and echelon grating were placed at a distance of about two metres from the end of the B tube, and its end-on image projected on the slit with a lens of 3 cms. diameter and 20 cms. focus.

This disposition is necessary if it is desired that every portion of a long tube contributes equally to the illumination of the instrument, as I have pointed out in previous papers. The tubes were excited independently by means of two high potential transformers.

Fig. 1.



With A moderately excited, so that the two components of H_α showed well separated in the echelon, it was found impossible to reduce their intensity or cause reversal by a feeble discharge in B. If, however, the current in A was augmented until the components fused together, and a current of equal intensity passed through B, H_α became a wide hazy line with two distinct darker lines in the position previously occupied by the two components. It was then found that the reversal of the two components could be effected without employing the tube B at all, by merely increasing still further the current in A. In other words, self-reversal appeared under conditions precluding the existence of an absorbing layer under physical conditions different from those of the emitting layer.

By no current adjustment could the reversed components be made really dark. They were dark only in comparison to the very bright field on which they were projected.

The reversal takes place in the following way I believe. It is well known that the intensity of the light emitted by a gas which both emits and absorbs a radiation of given wave-length increases as the depth of the radiating layer increases, reaching a final maximum value defined by $\frac{E}{A}$, beyond which point a further increment in the thickness of the layer contributes nothing to the illumination. This is the illumination due to a layer of infinite thickness, but in practice we have a value practically equal to this with a depth of moderate thickness, say from 20 to 50 cms. in the case of powerfully excited hydrogen gas.

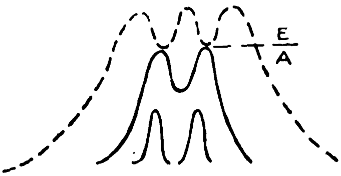
As I pointed out about twenty-five years ago, it is due to this circumstance that a hydrogen tube appears white or blue-white when viewed end-on and purple when viewed through the side.

With a layer of fixed thickness as in our vacuum tube we can bring the intensity up to its maximum value (viewed end-on) by merely augmenting the current. It is a little easier, however, to think of the thing in terms of increasing thickness.

As we increase this the intensity of the components of H_α increases, at first rapidly, and then more slowly, finally reaching a maximum value beyond which there is practically no further increase no matter how much we increase the thickness. This intensity $\left(\text{defined by } \frac{E}{A}\right)$ is the intensity of the *dark* lines which we observe when we further increase the thickness, and cause self-reversal. To see how this comes about we have only to assume that the absorption is less, in proportion to the emission for wave-lengths differing slightly from those of the two monochromatic components of H_α, in other words the ratio $\frac{E}{A}$ has a higher value for the *edges* of the lines than for the cores. Representing the intensity increase corresponding to increased thickness by curves in the usual manner, we have the phenomenon of reversal pictured in fig. 2. Curves 1, 1 the two components of H_α for a thin layer, curves 2, 2 for a layer of moderate thickness, showing the cores of the components at their maximum intensity, and curve 3 showing the reversal with dark lines of the same intensity as the bright lines of curve 2.

Previous investigations on the reversal of the hydrogen lines have been made with a source giving a very bright and more or less continuous spectrum, *e.g.* a fine capillary filled with hydrogen at rather high pressure, or a spark under water, the light being then passed through a tube filled with hydrogen at low pressure and moderately excited. The former arrangement was employed by Ladenburg, and my impression is that certain of his results led him to believe that the ratio $\frac{E}{A}$ varied with the wave-length. This conclusion was questioned by others at the time, but the observations reported in this paper appear to confirm it. The widening of the hydrogen lines with increasing current density is attributed by Merton to a Stark effect resulting from the electric fields of neighbouring atoms, and I am inclined to agree with him that the type of reversal with which we are dealing will have to be explained by taking this effect into account.

Fig. 2.



The peculiarity of hydrogen seems to lie in the fact that, at least under the conditions described, it is impossible to *reduce* the intensity of the lines by passing the light through a layer of less powerfully excited gas, the latter contributing always more light than it absorbs. No matter how feeble the excitation an actual darkening of the lines seen through the gas can never be detected. This behaviour of the gas is due, I imagine, to the circumstance that we are working with it in the molecular condition. As I showed in an earlier paper, if we operate with dry hydrogen, and free the walls of the tube from adsorbed water vapour, it is possible to excite the tube with a heavy current and obtain only the secondary spectrum, with no trace at all of the Balmer lines.

It may very well turn out that if we have only atomic hydrogen in the absorption and excite it at the lowest possible potential, the conditions for absorbing the light of the Balmer lines may be better realized.

This could be investigated with a long straight tube with three electrode bulbs instead of four as in fig. 1, the central electrode being connected to one pole of the transformer, and the end electrodes to the other, the one terminating the absorption tube through a very high resistance. A stream of atomic hydrogen will then flow continuously from the powerfully excited tube into the absorption tube, where it is again excited by a lesser potential.

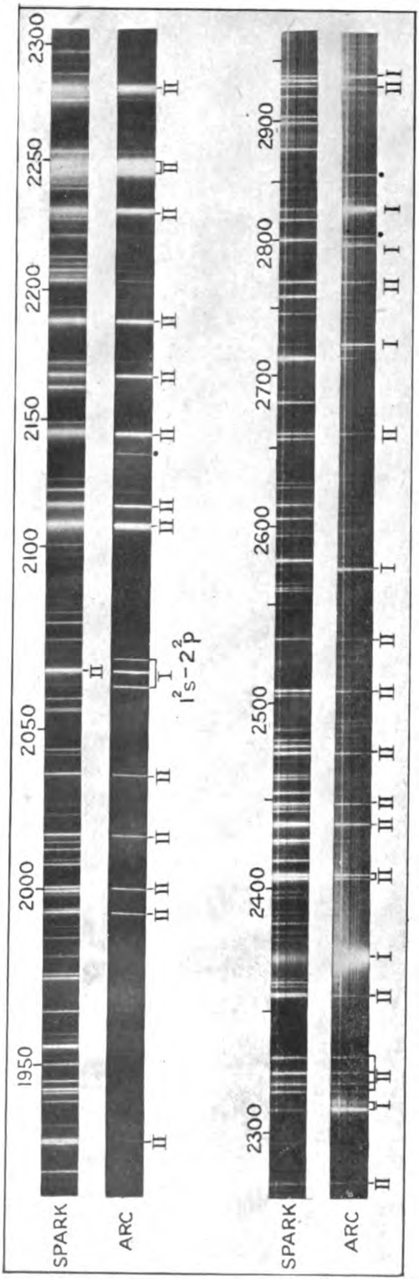
Several years ago, when working with atomic hydrogen I found that, if a small discharge tube was placed in circuit with the tube leading from the main discharge tube to the pump, it could be kept permanently filled with atomic hydrogen, which flowed out of the line of discharge to the pump. If the small tube was operated by a coil giving a very minute spark, the colour of the discharge was white, if no current was passing in the main tube, but purple (Balmer lines only) the moment the main tube was excited. The atomic hydrogen gradually passes back into molecular, owing to catalysis by the walls, as it passes down the tube, so that it is important to have the second tube as close as possible to the main discharge.

The self-reversal described in the earlier part of the paper I have seen only with an echelon, a twenty-plate one by Hilger, with the plates in optical contact. No trace of it appeared with either of the very fine quartz Lummer-Gehrke plates also by Hilger. N. A. Kent and I looked for it in vain in a much larger Lummer plate of glass, but saw it distinctly in his large glass echelon, the plates of which were not in optical contact. The phenomenon resembled so strongly the "grid-structure" shown by echelons of this type, that I was inclined to agree with him at the time, that it might be spurious (*i. e.* instrumental), but Dr. McCurdy and I observed it this winter with another echelon (optical contact) which we borrowed from Princeton, so I feel sure that it is real. Its failure to appear with the Lummer plate is probably due to some peculiarity of the intensity curve of the interference pattern of that instrument.

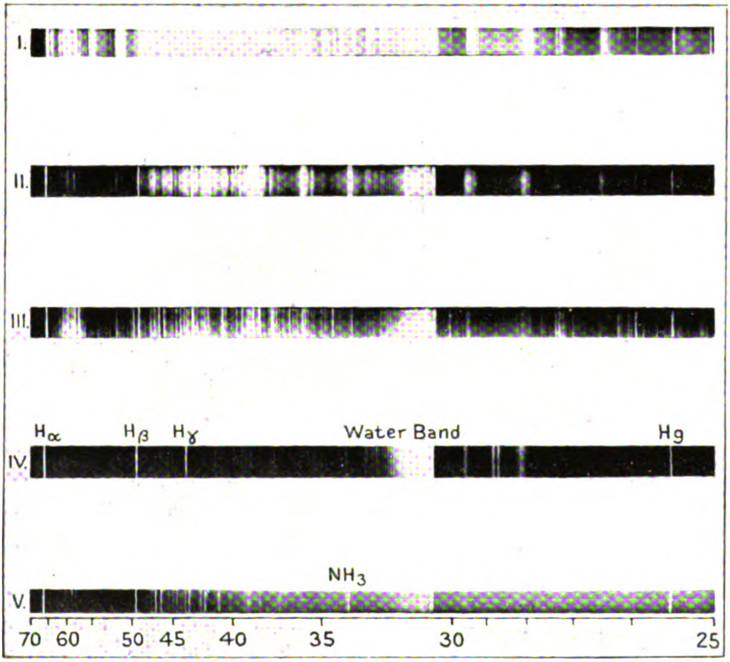
[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

BEALS. Phil. Mag. Ser. 7. Vol. 2, Pl. XIV.

SPECTRUM OF SILVER.



I. Arc Lines of Silver. II. Lines of Singly-ionized Silver.



Residual Gas { I. Arc.
II. Glow.

Hydrogen …… { III. Arc showing Balmer Series and Secondary lines.
IV. Glow. Water band prominent.
V. Glow. Water band disappearing.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

NOVEMBER 1926.

LXXX. *The Theory of the Vane Anemometer.*

By E. OWER, *A.C.G.I., B.Sc.* (*National Physical Laboratory*)*.

1.1. ALTHOUGH the vane anemometer has been in fairly common use for a considerable time, its behaviour has not hitherto been subjected to theoretical treatment, and consequently does not appear to be completely understood. As a means of measuring wind speed, more particularly, perhaps, in the range of low speeds where such small pressures are set up by the motion that their accurate determination becomes a matter of considerable difficulty, its simplicity renders it an exceedingly useful instrument, and if properly used it is capable of giving all the precision ordinarily required.

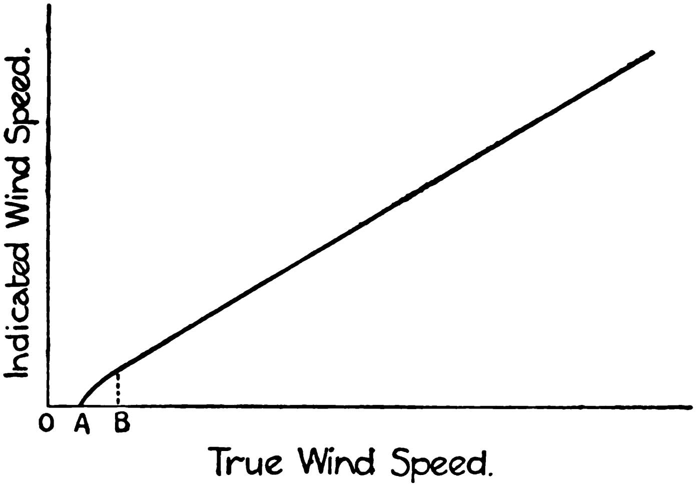
1.2. Before proceeding to a detailed analysis, we shall find it useful, in order to define the problem for consideration, to examine briefly the construction of the instrument. It consists, as is well known, of a number of flat light vanes, mounted on radial arms rigidly attached to a common spindle. The latter is placed along the wind direction and the vanes are inclined to the wind in such a manner that a torque is produced which causes them to rotate in a path perpendicular to the wind direction and at a speed which is a definite function of the wind speed. The motion of the spindle is communicated by suitable gearing to a pointer moving over a graduated dial. Normally, the dial is graduated in feet, and experience has taught manufacturers of these instruments how to proportion the various dimensions, vane inclinations, and gearing ratios so that the number of feet indicated on the dial in unit time is more or less equal to the distance traversed by the wind in the same time, *i. e.*, to the wind speed.

---

* Communicated by Mr. R. V. Southwell, F.R.S.

1.3. It will be apparent from the foregoing remarks that the speed of rotation of a given set of vanes will be determined not only by the wind speed, but also by the mechanical friction introduced at the spindle bearings and by the gearing. In the ideal case where friction is entirely absent, the curve of indicated wind speed against true wind speed will be a straight line passing through the origin (this is shown below, equation (2)) whose slope will be determined by the inclination of the vanes to the wind direction. In practice, however, friction has an appreciable effect, especially at low speeds when the wind forces on the vanes are small, and the usual calibration curve of a vane anemometer is as shown in fig. 1. At high speeds the curve in nearly every case exhibits no sensible departure from linearity, but at low speeds it bends over somewhat in the manner shown, the abscissa OA representing the true wind speed at which the vanes just commence to turn. The values of the wind speed corresponding to OA and to OB (above which the curve is linear) vary, as is to be expected, with different instruments; in a very sensitive anemometer specially designed for use at low speeds OA was

Fig. 1.



found to be about 0·5 feet per second, and OB about 1·0 feet per second.

1.4. This brief exposition of the characteristics of these instruments serves to define the limitations to which they are subject. It is often stated that vane anemometers are unreliable and give inconsistent readings which cannot be explained. The writer has, however, had considerable experience with the instruments, which certainly does not bear out these remarks. It appears probable that trouble frequently arises through the use of an instrument to measure wind speeds for which it is not suitable. It is not ordinarily advisable, for example, to attempt to measure speeds less than OB, which fall on the lower curved part of the calibration curve. On the other hand, if the speed is too high the vanes may suffer a permanent angular distortion which will cause a corresponding permanent alteration in the calibration curve. Most makers supply an instrument for general use which may safely be used for speeds ranging from 5 or 10 to 50 feet per second. For speeds higher than this special instruments of heavier construction can be obtained; for lower speeds instruments of the form designed by the writer * may be used with advantage, and will be found to give consistent readings down to about 0·6 feet per second.

1.5. A further point which must be remembered is that every instrument must be calibrated in a wind tunnel or on a whirling arm where the wind speed relative to the vanes can be regulated and measured by independent means. It is exceptional for two instruments made to the identical pattern and dimensions to have identical calibration curves.

2.1. In a theoretical discussion of the vane anemometer we have to consider a number of conditions. The relation between indicated and true speed shown by the curve of fig. 1 holds only for the case in which the instrument is placed in a steady wind, whose speed is uniform across the whole vane circle. In practice, however, these conditions are not usually realized, and we have the following three cases to consider:—

(*a*) Readings obtained in a fluctuating wind.
(*b*) Effect of variation of air density.
(*c*) Readings obtained when the wind speed varies across the vane circle.

---

* A description of this instrument appeared in the 'Journal of Scientific Instruments,' vol. iii., January 1926, p. 109.

2.2. EQUATIONS OF MOTION.

Notation.

F = air force on blade.
T = frictional torque.
Q = wind torque.
V = wind velocity.
v = linear tangential velocity of centre of pressure of blades.
$\overline{V} = \sqrt{V^2+v^2}$ = velocity of wind relative to blade.
n = rotational speed of blades.
A = area of one blade.
D = outside diameter of blade circle.
m = number of blades.
r = distance of centre of pressure of blade from axis of rotation.
ρ = air density = $\frac{\text{weight per unit volume}}{g}$.
N = rotational speed of pointer.
C = gearing constant, such that $N = Cv$.
K = wind force coefficient (see below).
θ = inclination of blade to wind direction.
ϕ = inclination of blade to relative wind (= "incidence" of blade).
γ = angle of resultant wind force on blade to relative wind direction.
I = total amount of inertia of all blades about axis of rotation.
g = acceleration due to gravity.

(i.) *Fundamental Equation.*

The anemometer may be regarded as a windmill, and aerodynamic theory has established the fact that for a windmill the wind torque Q may be written

$$\frac{Q}{\rho V^2 D^3} = f\left(\frac{nD}{V}\right), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $f(nD/V)$ represents some function of (nD/V) which has to be determined.

(ii.) *Equations for Particular Cases.*

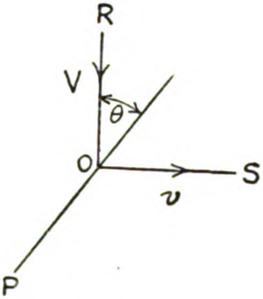
(a) *Mechanical Friction Absent.*

Let PQ (fig. 2) represent one blade inclined at an angle θ to the wind, and let O be the centre of pressure of the blade. (It should be noted that the blade is rotating in a circular path perpendicular to the plane of the paper.) The blade PQ will move instantaneously along OS, perpendicular to the wind direction RO, with a velocity v such that the resultant of V and v lies along QP,

i. e. $$v = \mathrm{V} \tan \theta,$$

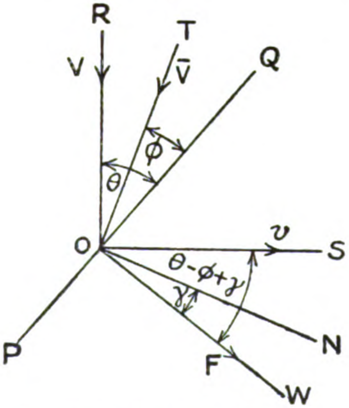
and $$\mathrm{N} = \mathrm{C}v = \mathrm{CV} \tan \theta. \quad . \quad . \quad . \qquad . \quad (2)$$

Fig. 2.



In this case, therefore, the calibration curve of the instrument will be a straight line passing through the origin.

Fig. 3.



(b) *Mechanical Friction Present.*

The velocity diagram now becomes more complicated, and it is necessary to consider the forces acting on the blade.

PQ will still move along OS perpendicular to the wind direction but at a lower speed v so that the resultant of V and v, i.e., the wind speed $\overline{V}$ relative to the blade, will now be inclined at an angle ϕ to the plane of the blade. The blade now becomes a flat plate inclined to the wind at an angle of incidence ϕ, and there will be a resultant force F on the blade acting along OW inclined at an angle γ to ON the normal to the relative wind direction. The component of F along OS multiplied by the distance of O from the centre of rotation and by the number of blades, supplies the torque which overcomes the resisting torque due to mechanical friction.

Now from experiments on the forces acting on flat plates in moving currents of air we have the equation

$$F = K\rho V^2 A\alpha,$$

where K is a numerical coefficient depending on the incidence α of the plate, and the other symbols have the significance tabulated in the list above.

Neglecting the inflow factor (*i. e.*, slowing up of the air entering the vane circle) and mutual interference between the blades *, we may therefore write for the blade under consideration

$$F = K\rho\overline{V}^2 A\phi.$$

Resolving along OS, putting $\overline{V}^2 = V^2 + v^2$, and equating the wind torque to the frictional torque, we therefore have for steady motion

$$T = K\rho\phi A(V^2 + v^2)mr\cos(\theta - \phi + \gamma). \quad . \quad . \quad (3)$$

Also

$$v = V\tan(\theta - \phi), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

so that, substituting the value of ϕ from (3) in (4), we have

$$v = V\tan\left[\theta - \frac{T}{K\rho A(V^2 + v^2)mr\cos(\theta - \phi + \gamma)}\right]. \quad . \quad (5)$$

The utility of equation (5) will be apparent later when we consider the effect of variation of density.

From consideration of (4) we see that at high speeds when the relative effect of friction is small in comparison with the wind forces, ϕ is small compared with θ and the calibration curve of the instrument will be practically linear. At low speeds ϕ becomes large compared with θ, and v will be zero at a certain low value of V when ϕ becomes equal to θ.

---

* The construction of the instrument and the conditions under which it works are such as to warrant the assumption that both these effects will be small.

2.3. CALCULATION OF THE MECHANICAL FRICTION TORQUE T.

A knowledge of T is required for the solution of the first and third of the problems stated above (see 2.1). Obviously, the mechanical friction will depend upon the construction of the anemometer so that it cannot be computed from first principles ; it has to be determined separately for every instrument by experiment. The necessary tests, however, are simple and comprise only a calibration to establish the relation between v and V for a number of values of the wind speed V. By the use of equations (3) and (4) T can then be calculated for different values of V, as follows.

Fig. 4.

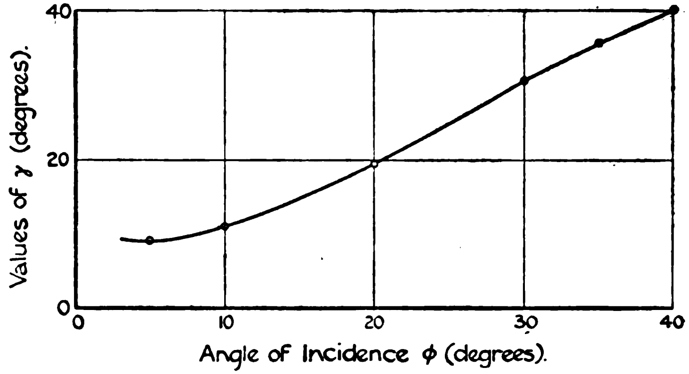
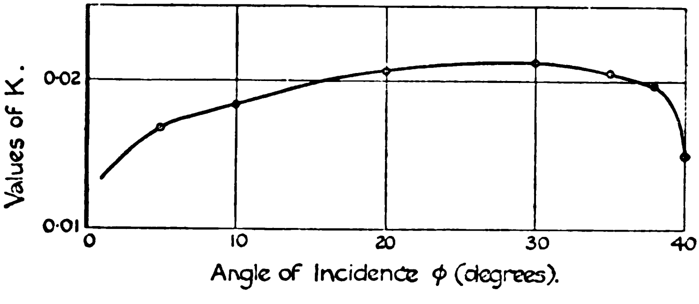


Fig. 5.



For a given V, the value of v is known from the calibration curve, so that ϕ can be determined from equation (4), θ being a measurable dimension in the instrument. The angle ϕ now represents the effective incidence of the blade for the conditions under consideration, and K and γ can therefore be determined from the aerodynamic characteristics of flat plates found experimentally by G. Eiffel *. For convenience, these quantities are reproduced, for the case of square plates,

---

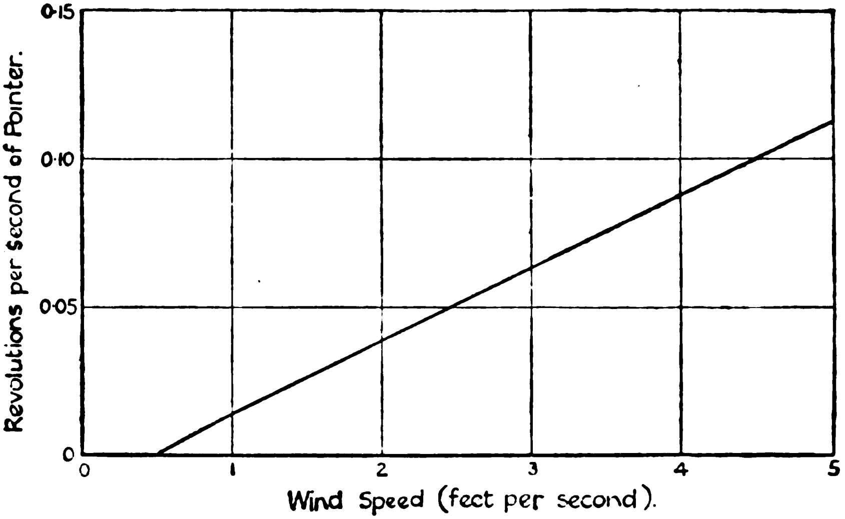
* 'La Résistance de l'Air et l'Aviation,' p. 134.

in figs. 4 and 5. (It is sufficiently close for our purpose to take square plate characteristics.) All the quantities in equation (4) are now known with the exception of T, which can therefore be calculated.

Calculations of T have been made in this manner for the writer's low speed vane anemometer mentioned above *. The

Fig. 6.

Calibration Curve for Low-Speed Anemometer.



calibration curve of this instrument is shown in fig. 6, and its mechanical constants are as follows:—

$A = 0{\cdot}007$ sq. feet.

$D = 0{\cdot}312$ feet.

$m = 8$.

$r = 0{\cdot}125$ feet.

$C = 0{\cdot}0254$.

$I = 192 \times 10^{-8}$ slugs ft.^{2}

ratio $\dfrac{\text{revs. of pointer}}{\text{revs. of vanes}} = \dfrac{1}{50}$.

For steady motion $Q = -T$, and the values of T obtained in the manner just indicated were inserted in equation (1), and a curve of $\dfrac{Q}{\rho V^2 D^3}$ against $\dfrac{nD}{V}$ was plotted. This curve

---

* *Loc. cit.*

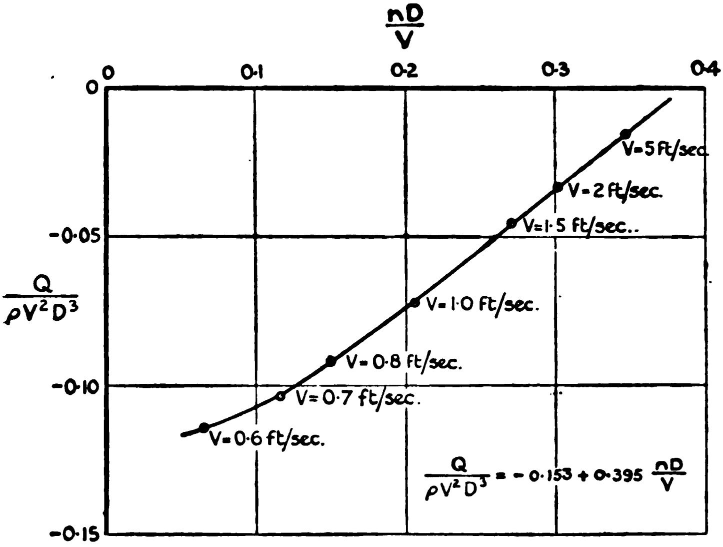
is reproduced in fig. 7; it will be seen that above $V = 1$ foot per second the curve is linear and can be expressed in the form

$$\frac{Q}{\rho V^2 D^3} = -0{\cdot}153 + 0{\cdot}395\frac{nD}{V}, \quad . \quad . \quad . \quad (6)$$

so that, incidentally,

$$f\left(\frac{nD}{V}\right) = -0{\cdot}153 + 0{\cdot}395\frac{nD}{V}.$$

Fig. 7.



It appears, therefore, that over the linear part of the calibration curve we may write

$$\frac{Q}{\rho V^2 D^3} = a + b\frac{nD}{V}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where *a* and *b* are constants, and this result may be expected to apply, in the region of linearity, to all instruments, the values of *a* and *b* varying from one to another.

3.1. EFFECT OF A FLUCTUATING AIR SPEED.

In order to investigate analytically the effect of a fluctuating wind speed, we may assume that V at any time *t* is given by the simple harmonic relation

$$V = V_0(1 + \lambda \sin pt), \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where V_0 is the value of V at time t_0.

We will imagine this fluctuating speed suddenly impressed upon the anemometer which was previously rotating at a steady rate n in a steady wind of speed V_0.

From equation (7), we have, at time $t = 0$

$$Q_0 = \rho V_0^2 D^3 \left(a + b\frac{n_0 D}{V_0}\right),$$

and at time $t = t$ shortly after

$$Q_1 = Q_0 + q = \rho(V_0 + v)^2 D^3 \left\{ a + b\frac{n_0 + n}{V_0 + v} D \right\},$$

where q, v, and n are small changes in Q_0, V_0, and n_0 respectively.

Hence

$$\begin{aligned}\frac{q}{\rho D^3} &= 2aV_0 v + av^2 + bD(V_0 + v)(n_0 + n)\\ &= bD(V_0 + v)n + v(2aV_0 + bDn_0) + av^2,\end{aligned}$$

and putting $v = \lambda V_0 \sin pt$, we have

$$\begin{aligned}\frac{q}{\rho D^3} = bDV_0(1 + \lambda \sin pt)n + \lambda V_0(2aV_0 + bDn_0) \sin pt\\ + a\lambda^2 V_0^2 \sin^2 pt.\end{aligned}$$

Hence the equation of motion for the rotation in a fluctuating wind of the assumed nature becomes

$$\begin{aligned}\frac{2\pi I}{\rho D^3} \cdot \frac{dn}{dt} + bDV_0(1 + \lambda \sin pt)\, n = -(2aV_0 + bDn_0)\lambda V_0 \sin pt\\ - a\lambda^2 V_0^2 \sin^2 pt,\end{aligned}$$

or

$$\frac{dn}{dt} + \alpha(1 + \lambda \sin pt)n = \beta \sin pt + \gamma \sin^2 pt, \quad . \quad (9)$$

where

$$\left.\begin{aligned}\alpha &= \frac{bDV_0\rho D^3}{2\pi I},\\ \beta &= -\frac{\lambda V_0(2aV_0 + bDn_0)\rho D^3}{2\pi I},\\ \text{and} \quad \gamma &= -\frac{a\lambda^2 V_0^2 \rho D^3}{2\pi I}.\end{aligned}\right\} \quad . \quad . \quad . \quad (9a)$$

The solution of (9) is

$$ne^{\left(t - \frac{\lambda}{p}\cos pt\right)} = \int (\beta \sin pt + \gamma \sin^2 pt) e^{\alpha\left(t - \frac{\lambda}{p}\cos pt\right)} dt + C_1. \quad . \quad . \quad . \quad (10)$$

This solution cannot be reduced further without making certain assumptions based on practical considerations. We have assumed that the wind speed varies according to a sine law about a mean value V_0, but have not yet assigned magnitudes to the amplitude or period of the variation. In practice, the frequency of the fluctuations in an artificial air current is of the order of one or two per second, and we may further justifiably suppose that some effort is being made to maintain the speed reasonably constant (we must exclude natural winds from consideration), so that it is unlikely that the speed will vary by more than ± 10 per cent. from the mean. We will therefore assume that the frequency is 2 per second (*i.e.*, the periodic time is 1/2 sec.) and the amplitude ± 10 per cent. of the mean speed. Hence in equation (8) we have

$$p = \frac{2\pi}{1/2} \quad \text{and} \quad \lambda = 0{\cdot}1,$$

i. e.,
$$\frac{\lambda}{p} = 0{\cdot}008.$$

Equation (10) then becomes

$$ne^{a(t-0\cdot008\cos pt)} = \int(\beta\sin pt + \gamma\sin^2 pt)e^{a(t-0\cdot008\cos pt)}\,dt + C_1.$$

Now the maximum value of $0{\cdot}008\cos pt$ is $0{\cdot}008$, so that when $t = 0{\cdot}8$, *i. e.*, before the motion has proceeded for one second, this term becomes less than 1 per cent. of t, and afterwards becomes relatively smaller. It is therefore legitimate to neglect $0{\cdot}008\cos pt$ in comparison with t, and we may write, with sufficient accuracy,

$$ne^{at} = \int(\beta\sin pt + \gamma\sin^2 pt)e^{at}\,dt + C_1,$$

the right-hand side of which can now be integrated, giving, after reduction,

$$n = \frac{\beta(\alpha\sin pt - p\cos pt)}{\alpha^2 + p^2} + \frac{\gamma(\alpha^2 + 4p^2 - \alpha^2\cos 2pt - 2\alpha p\sin 2pt)}{2\alpha(\alpha^2 + 4p^2)} + C_1e^{-\alpha t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The value of the constant C_1 can be obtained by putting $n = 0$ when $t = 0$ since n is the change in the rotational speed of the vanes from its value at the commencement of the fluctuating motion. We are, however, not concerned with the value of C_1 since the term $C_1e^{-\alpha t}$ represents a quickly damped initial disturbance *. The motion therefore rapidly assumes a steady periodic character represented by the first two terms of (11), and the average value of n can easily be seen to be $\gamma/2\alpha$. Substituting the values of γ and α given above (9a), we obtain finally :—

$$\text{Average value of rotational speed above mean} = -\frac{a\lambda^2}{2bD}V_0,$$

where V_0 represents the mean about which the wind speed fluctuates, and the mean rotational speed will be that taken at speed V_0 from the calibration curve obtained in a steady wind.

In other words, this implies that the anemometer, when placed in a wind fluctuating in the assumed manner about a mean value V_0, will rotate at an average rate higher by $\gamma/2\epsilon$ than the rate at which it would rotate in a steady wind speed V_0 ; *i.e.*, an anemometer in a fluctuating wind gives readings in excess of the mean wind speed.

It will be seen that the quantity $\frac{\gamma}{2\alpha}\left(= -\frac{a\lambda^2}{2bD}V_0\right)$ is independent of the period of the fluctuations in the wind speed and of the moment of inertia of the vanes. It appears that these quantities will merely determine the lag of the periodic motion of the vanes behind that of the wind, whilst the mean amplitude of the motion of the vanes is affected only by the amplitude of the variations of the wind speed. (An inspection of (11), however, shows that the *actual* value of n at any time is influenced by p and I ; it is only the *average* value of n that is independent of these quantities.)

To obtain some idea of the magnitude of the excess reading obtained in a fluctuating wind, we may apply this result to the low-speed anemometer to which reference has already been made. The values of a and b are given in equation (6), and the value of D will be found in the list of constants for this instrument. The value of $-\frac{a\lambda^2}{2bD}V_0$ will be found to become $0{\cdot}0062\ V_0$ (a is negative), assuming λ as before to be 0·1. We can now draw up the following table in which the value of $0{\cdot}0062\ V_0$ is shown for various values of V_0 ; the value of n_0 corresponding to each value of V_0 was derived from the calibration curve obtained in a steady wind (see fig. 6), and the last column, in which $0{\cdot}0062\ V_0$ is expressed as a percentage of n_0, shows the percentage increase in the readings of the instrument when placed in the fluctuating wind of mean speed V_0. If the instrument read the true mean speed, this percentage would be zero ; actually it is not zero, but is always less than 1 per cent. As the assumed value of λ is probably on the high side, if we consider only those cases in which measurements are made of the speed of air currents produced by fans running at speeds which are intended to be maintained constant, it appears legitimate to assume that in practice the effect of a fluctuating wind on the readings of an anemometer may usually be neglected.

---

* In the case of the author's low-speed anemometer this disturbance is reduced to 1/10 of its initial amplitude in just over 3 seconds when $V_0 = 1$ foot per sec.., and in correspondingly shorter times as V_0 increases.

V_0 Feet per sec.	$0{\cdot}0062\ V_0$ revs. per sec.	n_0 revs. per sec.	Percentage error in reading of anemometer.
1	0·0062	0·660	0·94
2	0·0124	1·93	0·64
3	0·0186	3·15	0·59
4	0·0248	4·31	$0{\cdot}57_5$
5	0·0310	5·56	0·56

3.2. EFFECT OF VARIATION OF AIR DENSITY.

From equations (3) and (4) it will be seen that the value of ϕ depends partly on the air density ρ, so that the calibration of the anemometer will vary somewhat with ρ. Equation (2), however, which gives the calibration curve when mechanical friction is neglected, shows that in this case ρ does not appear. It seems probable, therefore, that at the higher wind speeds, when frictional forces are relatively small compared with the air forces, the effect of variations in ρ will be small and may be neglected. But if an anemometer is employed for the measurement of low wind speeds, for which purpose it has an eminent superiority over other instruments, it is necessary to investigate more closely the effect of a variation in ρ. Errors may then arise on account of the fact that when measurements are being taken the air density may differ somewhat from that existing at the time when the instrument was calibrated, for which conditions only the calibration curve is strictly valid. The writer has already investigated this effect in a communication to the 'Journal of Scientific Instruments'*, but for the sake of completeness he has thought it advisable to reproduce it briefly here. He wishes to acknowledge the courtesy of the Editor of that Journal for permitting him to do so.

Equations (3), (4) and (5) are employed for this purpose. Let suffixes 0 refer to the conditions under which the instrument was calibrated, and suffixes 1 to the conditions under which measurements are being made, *i e.*, when the air density has changed from ρ_0 to ρ_1. For any given value of V, v_0 can be obtained from the calibration curve, and the frictional torque T_0 and ϕ_0 can be obtained from equations (3) and (4). The new value of ϕ when the density is ρ_1 is given by

$$\phi_1 = \frac{T_1}{K_1\rho_1 A(V^2+v_1^2)mr\cos(\theta-\phi_1+\gamma_1)} . \quad . \quad (12)$$

Now, in practice the air density does not frequently change by more than about 3 per cent., although extreme variations of over 4 per cent. are occasionally experienced. In any case, the change is always small, so that we can assume that the frictional torque is unchanged, *i. e.*, that $T_1 = T_0$. We therefore have the two equations

$$\phi_1 = \frac{T_0}{K_1\rho_1 A(V^2+v_1^2)mr\cos(\theta-\phi_1+\gamma_1)} \quad . \quad (13)$$

and

$$v_1 = V\tan(\theta-\phi_1), \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

which are theoretically sufficient for the determination of ϕ_1 and v_1 if the small variations in γ are neglected.

Actually, however, the solution is complicated, and it is quicker to resort to the following method of successive approximation :—Since we are dealing with small changes, a first approximation to the value of ϕ_1 is obtained by assuming that $v_1 = v_0$, $K_1 = K_0$, and $\gamma_1 = \gamma_0$. Equation (13) then becomes, if the value of T_0 from (3) is inserted,

$$\phi_1 = \frac{\rho_0}{\rho_1}\phi_0.$$

By substituting this value of ϕ_1 in (4) a first approximation to the value of v_1 is obtained. We can now calculate $(V^2+v_1^2)$ and get first approximations to the values of K_1 and γ_1, and, by putting these in (13), obtain a second approximation to ϕ_1 and hence to v_1. The process can be repeated a further stage, if desired, but two approximations will usually be found to be sufficient.

---

* *Loc. cit.*

The following table shows the results of calculations made in this manner for the author's low speed anemometer, on the assumption that ρ is 3 per cent. in excess of its value at which the calibration curve was obtained.

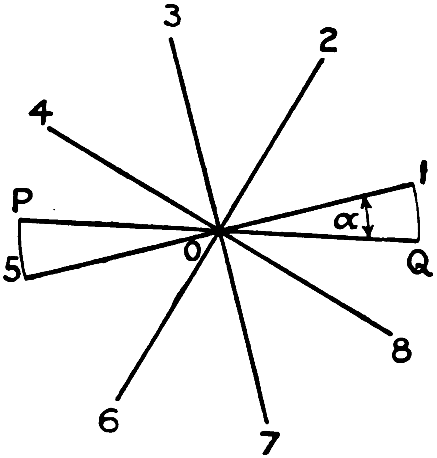
Wind speed V. Feet per sec.	Air density.		Percentage change in v $= 100 \times \frac{v_1 - v_0}{v_0}$.
	ρ_0.	$1{\cdot}03\ \rho_0$.	
	Linear blade speed v_0. Feet per sec.	Linear blade speed v_1. Feet per sec.	
0·7	0·204	0·219	7·2
0·8	0·303	0·319	5·3
1·0	0·519	0·533	2·7
1·5	1·021	1·032	1·1
2·0	1·520	1·531	0·7
5·0	4·37	4·39	0·5

From these results it will be seen that the effect of variations in ρ may be appreciable at low speeds and should be considered for accurate work. Although the assumed change in ρ is somewhat on the high side, it should be pointed out that the instrument to which these results relate was specially designed for low speed work, the construction being carefully carried out with a view to reducing mechanical friction to a minimum. The table emphasizes the danger of using unsuitable instruments for low speed measurements and the desirability of measuring and recording the air density at which the instrument was calibrated and that obtaining during subsequent experiments at low speeds. For high speeds this refinement is unnecessary.

3.3. EFFECT OF A VARIATION IN WIND SPEED ACROSS THE VANE CIRCLE.

In general the distribution of velocity across a pipe along which air is flowing is not uniform, the velocity being higher at the centre than near the walls. It is well known that in order to determine the quantity of air flowing in such a case, the velocity has to be measured at certain definite radii, which are the mean radii of a number of imaginary concentric zones of equal area into which the pipe has to be divided in making measurements. The question therefore arises whether, when measurements are made by means of an anemometer, the instrument must be placed with its axis at the radii in question or at other points, the answer depending on whether or not the anemometer will rotate at the speed appropriate to the velocity of the filament of air at the centre of its disk or at a rate corresponding to some other wind speed.

Fig. 8.



In fig. 8 let O1, O2, O3, etc., represent the median lines of the eight blades of the anemometer (eight blades are almost invariably used) and let r be the radius to the centre of pressure of a blade. Let blade O1 be at an angle α to the reference line PQ, and let the velocity vary along PQ according to the relation

$$V = V_0(1+Ax+Bx^2), \quad . \quad . \quad . \quad . \quad (15)$$

where V is the velocity at any point along PQ, distant x from P where the velocity is V_0.

Also let PO = OQ = r.

Assuming the velocity distribution perpendicular to PQ to be uniform, *i.e.*, that the velocity at all points on a line perpendicular to PQ is the same, we can write down the velocities V_1, V_2, etc., of the air impinging on the centre of pressure of each blade as follows :—

$$\left.\begin{aligned}
V_1 &= V_0\left[1+Ar(1+\cos\alpha)+Br^2(1+\cos\alpha)^2\right],\\
V_2 &= V_0\left[1+Ar(1+\cos\overline{\tfrac{\pi}{4}+\alpha})+Br^2(1+\cos\overline{\tfrac{\pi}{4}+\alpha})^2\right],\\
V_3 &= V_0\left[1+Ar(1-\sin\alpha)+Br^2(1-\sin\alpha)^2\right],\\
V_4 &= V_0\left[1+Ar(1-\sin\overline{\tfrac{\pi}{4}+\alpha})+Br^2(1-\sin\overline{\tfrac{\pi}{4}+\alpha})^2\right],\\
V_5 &= V_0\left[1+Ar(1-\cos\alpha)+Br^2(1-\cos\alpha)^2\right],\\
V_6 &= V_0\left[1+Ar(1-\cos\overline{\tfrac{\pi}{4}+\alpha})+Br^2(1-\cos\overline{\tfrac{\pi}{4}+\alpha})^2\right],\\
V_7 &= V_0\left[1+Ar(1+\sin\alpha)+Br^2(1+\sin\alpha)^2\right],\\
V_8 &= V_0\left[1+Ar(1+\sin\overline{\tfrac{\pi}{4}+\alpha})+Br^2(1+\sin\overline{\tfrac{\pi}{4}+\alpha})^2\right].
\end{aligned}\right\}(16)$$

Let the anemometer rotate under the effect of this variable velocity at a linear speed $\bar{v}$ which would correspond, according to the calibration curve, to a wind speed $\bar{V}$. Then $\bar{V}$ and $\bar{v}$ will be such that the torque on the whole instrument rotating at this speed will be equal to the sum of the individual torques contributed by each blade.

Now from equation (3) we have

$$\text{Torque} = K\rho A\phi(V^2+v^2)mr\cos(\theta-\phi+\gamma).$$

Provided that the wind speed is such that the anemometer is rotating at a fair speed, *i.e.*, that we are working on a portion of the calibration curve some distance from B in fig. 1, no appreciable error will be introduced by assuming that ϕ, and hence also K and γ, are constant for all the blades, so that we may write

$$\text{Torque} = K'm(V^2+v^2).$$

The condition of total torque equal to sum of torques of all the blades is, therefore, expressed by the equation

$$8K'(\bar{V}^2+\bar{v}^2) = K'\{V_1^2+\bar{v}^2)+(V_2^2+\bar{v}^2)+\ldots+(V_8^2+\bar{v}^2)\},$$

i.e., $$8\bar{V}^2 = V_1^2+V_2^2+V_3^2+\ldots+V_8^2 = \Sigma V_1^2.$$

From equations (16) it will be found, after reduction, that

$$\Sigma V_1^2 = 8V_0^2\Big[(1+Ar+Br^2)^2 + \frac{r^2}{8}(4A^2+8B+24ABr+27B^2r^2)\Big],$$

which is independent of α and hence constant for all positions of the blades, so that

$$\overline{V} = V_0\sqrt{(1+Ar+Br^2)^2+\frac{r^2}{8}(4A^2+8B+24ABr+27B^2r^2)}. \quad . \quad . \quad . \quad (17)$$

In this equation $\overline{V}$ is, as we have seen, the wind speed indicated by the anemometer. If the instrument indicated the speed of the wind passing through the centre of its disk, the value of $\overline{V}$ would be $V_0(1+Ar+Br^2)$, so that it appears that the indicated wind speed is the speed of the air at some point along the radius of the anemometer.

To get some idea of the magnitude of the discrepancy, we must take numerical examples. Let us assume, in order to fix our ideas, that the wind speed given by equation (15) is V_0 at $P(x = 0$ in fig. 8) and rises to $2V_0$ at $Q(x = 2r)$, and that at $x = r$, the centre of the disk, $V = 1{\cdot}8V_0$. We can now calculate the values of A and B and, by inserting these in equation (17), we get

$$\overline{V} = 1{\cdot}69V_0,$$

which is 6 per cent. less than the velocity at the centre of the disk, and is the velocity at the point $x = 0{\cdot}81\,r$, instead of at $x = r$.

If the diameter of the anemometer is small compared with that of the pipe, it will probably be sufficiently accurate to assume a linear variation of velocity across the disk of the form

$$V = V_0(1+Ar).$$

In this case, similar reasoning leads to the result

$$\overline{V} = V_0\sqrt{1+Ar)^2+\frac{A^2r^2}{2}},$$

and, on the assumption, as before, that the velocity at $x = 2r$ is twice the velocity at $x = 0$, we have

$$\overline{V} = 1{\cdot}54V_0 = \text{velocity at the point } x = 1{\cdot}08\,r,$$

i. e., $\overline{V}$ is 2–1/2 per cent. greater than the velocity at the centre of the disk.

In practice, provided the pipe diameter is reasonably large in relation to that of the anemometer, a distribution of velocity such as that assumed in both the above cases, in which the wind speed at the centre of pressure of a blade in one of its extreme positions is double its valne in the other, is probably of very rare occurrence, so that in general the errors in indicated wind speed will be less than those given above.

4.1. CONCLUSIONS.

The foregoing analysis serves to define the various conditions appropriate to the use of the vane anemometer, and to impose certain limitations thereon.

As regards the influence of a fluctuating wind speed, it would appear that no perceptible effect is normally to be anticipated from this cause. Judged by usual standards, a very unsteady wind speed would be required to cause the instrument to give readings markedly in excess of the mean speed.

Variations in the air density need be taken into account only when an instrument is used in the extreme lower end of its range for the measurement of very slow wind speeds. A statement of the air temperature and barometric pressure at which the instrument was tested should accompany the calibration curve of an anemometer intended for low speed work; the method of applying the necessary corrections is shown in the analysis.

It is important that instruments should be used only within the range for which they are intended. The ordinary anemometer is suitable neither for the measurement of very low wind speeds, nor for speeds in excess of about 50 feet per second. For the former work, special care in the design and construction is necessary if a satisfactory performance is to be obtained; reference has been made above to an instrument suitable for the measurement of low speeds. It is equally important that an anemometer should not be subjected to wind speeds higher than those for which it is designed; this point has already been emphasized in the introductory remarks of the present paper, see § 1.4.

The third problem which has been considered, namely the effect of a variation of wind speed across the anemometer disk, has an important bearing on measurements of air flow along pipes, where there is, in general, a variation in velocity across a section. It appears that, in order to avoid errors from this cause, the diameter of the anemometer should be fairly small in comparison with that of the pipe, so that the variation of speed across the instrument itself is small. Unless precautions are taken to equalise the velocity at different points along the pipe diameter if a marked variation originally exists, an anemometer should not be used in a pipe whose diameter is less than about 7 or 8 times that of the instrument.

If the above limitations and conditions are observed, vane anemometers can be used with confidence to give all the accuracy that is ordinarily required. It should be remembered that, as with all measuring instruments, the vane anemometer has its particular sphere of usefulness, and it should consequently not be condemned because it cannot be used to measure wind speed in all circumstances; there must obviously be cases in which other instruments, the pitot-tube for example, will be more suitable. As an adjunct to the pitot-tube, the vane anemometer is a very valuable instrument, and for the measurement of very low wind speeds it would appear to provide the most convenient means available.

LXXXI. *On Irrotational Flow past Two Intersecting Planes.*

By W. B. Morton, *M.A.*, *Queen's University, Belfast* [*].

IN a paper on the Electrification of two intersecting planes, published in this Magazine for February 1926 [†], it was shown that if the complex variables $z\zeta$ are connected by the equation

$$z = C\zeta^{-1}(\zeta - e^{i\alpha})^{1+k}(\zeta - e^{-i\alpha})^{1-k},$$

then the perimeter of unit circle, on the ζ-plane, corresponds on the z-plane to the two sides of two straight lines of finite length making with each other the external angle $k\pi$. Other points of the z-plane are represented on the interior of the circle. The relation was found by integrating the Schwarz differential equation, regarding the two lines as a collapsed quadrilateral. In the present note the same transformation is used to investigate the irrotational steady motion of a liquid past the planes, without formation of dead water; or, alternatively, the motion of the planes through liquid which is at rest at infinity. I have made drawings of the relative lines of flow for some directions in the particular case of two equal planes at right angles, the case which was examined in detail in the electrification problem. An expression is found for the couple exerted on the planes in the general case, and this is followed by a discussion of the positions of equilibrium of the planes relative to the stream, or of their possible steady motions through liquid.

---

[*] Communicated by the Author.

[†] Vol. i. p. 337.

The validity of the transformation given above can be verified by considering the variation of the argument of the expression in ζ as the point moves round the unit circle.

To make the values definite we lay it down that for points on the radii to $e^{i\alpha}$ and $e^{-i\alpha}$ the arguments of $(\zeta-e^{i\alpha})$ and $(\zeta-e^{-i\alpha})$ shall be $(-\pi+\alpha)$ and $(\pi-\alpha)$ respectively. The critical points are circumvented by small semi-circles drawn on the inner side of the circumference, and so their passage in the positive direction along the circle involves a decrease of π in the argument of the difference-terms. Thus the argument just before passing one of the points is $\frac{1}{2}\pi$ more than the value on the radius, and, just after passing it, $\frac{1}{2}\pi$ less. If $\rho\ \phi$ are polar coordinates in the ζ-plane, and ϕ runs from $-\pi$ to π, we obtain, for points on the circle $\rho=1$,

when $\quad -\pi<\phi<\alpha, \quad \arg(\zeta-e^{i\alpha}) = \frac{1}{2}(-\pi+\alpha+\phi)$

$\qquad\quad \alpha<\phi<\pi, \qquad\quad ,, \qquad\quad = \frac{1}{2}(-3\pi+\alpha+\phi),$

when $\quad -\pi<\phi<-\alpha, \quad \arg(\zeta-e^{-i\alpha}) = \frac{1}{2}(3\pi-\alpha+\phi)$

$\qquad\quad -\alpha<\phi<\pi, \qquad\quad ,, \qquad\quad = \frac{1}{2}(\pi-\alpha+\phi).$

If the constant C is omitted, these values give for the argument of z the following:

$$-\pi<\phi<-\alpha, \quad \arg z=(1-2k)\pi+k\alpha,$$

$$-\alpha<\phi<\alpha, \quad ,, \quad =-k\pi+k\alpha,$$

$$\alpha<\phi<\pi, \quad ,, \quad =-(1+2k)\pi+k\alpha.$$

Put $C=Ae^{ik(\frac{3}{2}\pi-\alpha)}$ where A is real *, and the arguments become

$$(1-\tfrac{1}{2}k)\pi$$

$$\tfrac{1}{2}k\pi$$

$$(1-\tfrac{1}{2}k)\pi-2\pi.$$

---

* By a slip this factor was given as $e^{ik\pi}$ in the former paper (top of p. 342). This did not affect the calculations for the symmetrical case for which $\alpha=\frac{1}{2}\pi$.

This gives two straight lines making an exterior angle $k\pi$ and placed so that the axis of η bisects their interior angle. The points $\phi=-\alpha$ and $\phi=\alpha$ on $\rho=1$ correspond to the inside and outside of the corner.

For a point on the right-hand plane, $-\alpha<\phi<\alpha$, the distance from the angle

$$r=|z|=4\mathrm{A}\sin^{1+k}\tfrac{1}{2}(\alpha-\phi)\sin^{1-k}\tfrac{1}{2}(\alpha+\phi),$$

$$dr/d\phi=2\mathrm{A}\sin^{k}\tfrac{1}{2}(\alpha-\phi)\sin^{-k}\tfrac{1}{2}(\alpha+\phi)(\sin\phi+k\sin\alpha).$$

So r is maximum when $\sin\phi=-k\sin\alpha$. The end of the line therefore corresponds to the value $\phi=-\beta$, where $\sin\beta=k\sin\alpha$ and the length is

$$4\mathrm{A}\sin^{1+k}\tfrac{1}{2}(\alpha+\beta)\sin^{1-k}\tfrac{1}{2}(\alpha-\beta).$$

For the end of the left-hand line we find in the same way $\phi=-(\pi-\beta)$ and the length

$$4\mathrm{A}\cos^{1+k}\tfrac{1}{2}(\alpha-\beta)\cos^{1-k}\tfrac{1}{2}(\alpha+\beta).$$

The parameter α is therefore given by the ratio

$$\text{right-hand length/left-hand length}$$

$$=\tan\tfrac{1}{2}(\alpha+\beta)\tan\tfrac{1}{2}(\alpha-\beta)\{\sin(\alpha+\beta)/\sin(\alpha-\beta)\}^{k}$$

with $\sin\beta=k\sin\alpha$.

Points near the origin on the ζ-plane correspond to distant points on the z-plane. As $\rho\longrightarrow 0$ the arguments of $(\zeta-e^{i\alpha})$ and $(\zeta-e^{-i\alpha})$ for any ϕ approach the radial values already assigned, $(-\pi+\alpha)$ and $(\pi-\alpha)$ respectively. The argument of z approaches the value $-k(\tfrac{1}{2}\pi-\alpha)-\phi$ *.

This is the limiting inclination to the axis of x of the curve $\phi=\text{const}$. The diagram given (*loc. cit.* p. 342) of the curves $\rho=\text{const.}$, and $\phi=\text{const.}$ for two equal lines at right-angles ($k=\tfrac{1}{2}$, $\alpha=\tfrac{1}{2}\pi$) can be taken to represent irrotational two-dimensional flow round two planes. We pass now to the question of steady flow past the planes.

Let u be the velocity potential and v the stream-function, and write $u+iv=w$. It is easy to show that the required solution is given by the equation

---

* Erroneously given as $k(2\alpha-\pi)-\phi$ in the former paper.

$$w=\mathrm{B}(e^{-i\gamma}\zeta+e^{i\gamma}\zeta^{-1})$$

with $$z=\mathrm{A}e^{-ik(\frac{\pi}{2}-\alpha)}\zeta^{-1}(\zeta-e^{i\alpha})^{1+k}(\zeta-e^{-i\alpha})^{1-k}.$$

Putting $\zeta=\rho e^{i\phi}$ and separating the real and imaginary parts of w, we have

$$u=\mathrm{B}(\rho^{-1}+\rho)\cos(\phi-\gamma)$$

$$v=-\mathrm{B}(\rho^{-1}-\rho)\sin(\phi-\gamma).$$

The stream-line $v=0$ is made up of the curve $\phi=\gamma$ and the two faces of the planes over which $\rho=1$. The direction of the undisturbed stream is thus $-k(\frac{1}{2}\pi-\alpha)-\gamma$.

We may find the distance at infinity between the stream-line $v=\mathrm{C}$ and a parallel line drawn through the point of intersection of the planes. When ρ is small the approximate values are

$$|z|=\mathrm{A}/\rho$$

$$\arg z=-k(\tfrac{1}{2}\pi-\alpha)-\phi-2\rho(\cos\alpha\sin\phi-k\sin\alpha\cos\phi).$$

For a distant point on the line

$$-\mathrm{B}(\rho^{-1}-\rho)\sin(\phi-\gamma)=\mathrm{C}$$

we have $$\phi=\gamma-\mathrm{CB}^{-1}\rho.$$

It follows that the required distance is

$$\mathrm{ACB}^{-1}+2\mathrm{A}(k\sin\alpha\cos\gamma-\cos\alpha\sin\gamma).$$

The calculation of the coordinates of points on the stream-line $v=\mathrm{C}$ is laborious, but a sufficiently accurate drawing of the curves of flow can be made by calculating values of ϕ for a succession of values of ρ and plotting directly on tracing-paper laid over the network of coordinate lines $\rho=$const. and $\phi=$const. as drawn to represent equipotentials and lines of force in the electrification problem.

I have drawn the lines of flow for a number of directions past two equal planes at right-angles, using the diagram of the previous paper as a basis. It will be sufficient to reproduce one case (fig. 1), that for a stream whose direction at infinity makes 30° with the axis of x. It will be noticed that the stream splits at the edge of the planes, although the limiting direction of the stream makes an angle of 15° with the plane. The other cases present similar features as regards the general arrangement of the stream-lines. Fig. 2 shows the points where the stream splits on the two planes for different directions of flow. The arrows can, of course, be reversed.

Fig. 1.

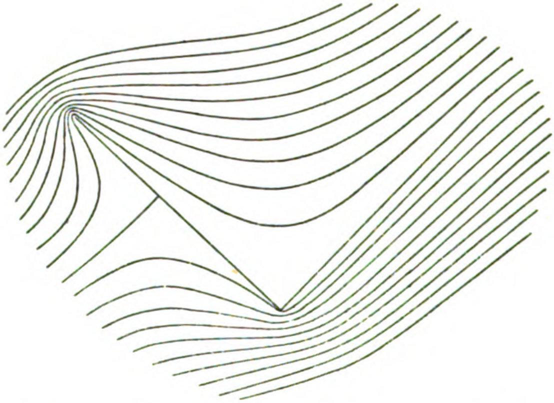
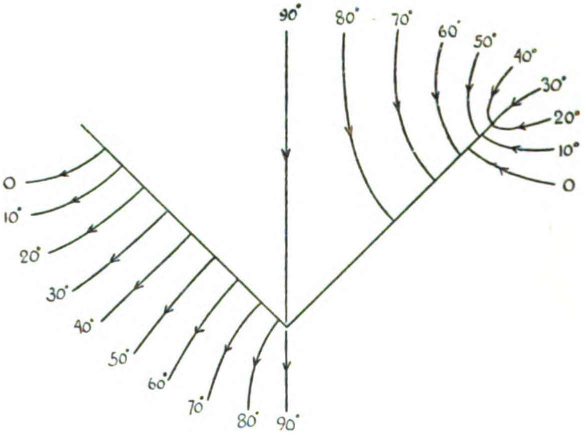


Fig. 2.



If q is the velocity at any point then q^{-1} is the modulus, and the inclination of q to the real axis the argument, of the complex quantity

$$\begin{aligned} dz/dw &= dz/d\zeta \times d\zeta/dw \\ &= \mathrm{A}e^{ik(\frac{3}{2}\pi-\alpha)}(\zeta-e^{i\alpha})^{k}(\zeta-e^{-i\alpha})^{-k} \\ &\quad \times(\zeta+e^{i\beta})(\zeta-e^{-i\beta})/\mathrm{B}\zeta(e^{-i\gamma}\zeta-e^{i\gamma}\zeta^{-1}). \end{aligned}$$

Putting $\zeta=0$, we see that the undisturbed velocity of the stream is $\mathrm{B}/\mathrm{A}=q_0$ say, and its direction is that of the line $\phi=\gamma$ at infinity, i. e., $-k(\frac{1}{2}\pi-\alpha)-\gamma$.

For points on the planes ($\rho=1$) we find

$$q=q_0\left|\sin(\phi-\gamma)\,.\,\sin^{k}\tfrac{1}{2}(\phi+\alpha)\,.\,\sin^{-k}\tfrac{1}{2}(\phi-\alpha)\,.(\sin\phi+\sin\beta)^{-1}\right|.$$

This vanishes at $\phi=\gamma$ and $\phi=-\pi+\gamma$, where the stream-line splits on the planes, and at $\phi=\alpha$ the inside of the corner. It is infinite at $\phi=-\alpha$, the outside of the corner, and at $\phi=-\beta$, $\phi=-\pi+\beta$, the tips of the planes.

When the forces exerted on the planes by the liquid are considered a result is found which at first sight seems to contradict the general theorem that a solid, in an irrotationally moving steady stream, without formation of dead water, is subject to a couple only. If the thrusts of the liquid on the planes act perpendicularly to them, it is evident that their resultant can vanish only when the two thrusts vanish separately. An examination of the integrals of the pressure as given by the above theory shows that this is not the case; so a definite resultant force appears to be exerted by the stream.

Without going into the integral expressions it is easy to see that the separate thrusts do not vanish by considering the limiting case, when the two planes flatten out into a single plane as k becomes zero. The points on the inner and outer sides of the angle then become opposite points on the two faces of the single plane which divide its breadth in the ratio $(1-\cos\alpha)$ to $(1+\cos\alpha)$. Obviously the thrusts on the two portions do not separately vanish for all values of α, and we are justified by considerations of continuity in inferring that the same is true when the two parts are inclined. In the case of a single plane the thrusts on the two parts are equal and opposite, and being parallel they form a couple, but in the case we are considering there is not this way of escape from a resultant force.

The explanation of the paradox is of course to be sought in the infinite velocities at the edges of the planes. The double plane is to be regarded as the limit approached by the boomerang-like figure, with rounded ends, formed by a closely fitting equipotential in the electrification problem. On the ends there will be a thrust, or rather defect of thrust, directed along the planes due to the high velocity round the ends. As the edges are sharpened into the planes these thrust-components do not vanish but approach a definite limit. There are thus forces along the planes which balance the forces on their faces, in accordance with the general dynamical theory.

By way of illustration of this point it will be sufficient to consider the well-known case of an elliptic cylinder as it shrinks to the plane strip between its foci. It is easy to show that, when the stream is oblique to the major axis, the component thrust-defect on each half of the section, in the direction of the major axis, approaches a finite limit.

We have $q^2 = q_0{}^2 e^{2a} \sin^2(\eta-\gamma)/(\cosh^2\alpha - \cosh^2\eta)$,

where q_0 is the velocity of the undisturbed stream, γ its inclination to the major axis, ($a \cosh\alpha$, $a \sinh\alpha$) the axes of the ellipse and η the excentric angle of a point on it. For the component along Ox of the thrust-defect on one side of the minor axis the value found is

$$\tfrac{1}{2}\rho q_0{}^2 \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} e^{2a} \sinh\alpha \sin^2(\eta-\gamma)\cos\eta \, d\eta/(\cosh^2\alpha - \cos^2\eta)$$

$$= \rho q_0{}^2 e^{2a} \{\cos 2\gamma \sinh\alpha + (\sin^2\gamma \cosh^2\alpha$$

$$- \cos^2\gamma \sinh^2\alpha) \tan^{-1} \operatorname{cosech}\alpha\};$$

when $\alpha = 0$ this becomes $\tfrac{1}{2}\pi\rho q_0{}^2 \sin^2\gamma$, so a plane strip set obliquely in a stream is subject to a kind of hydrodynamical tension along its edges.

The couple acting on the planes can be found by taking the moments of the normal pressures round the angle. The extra forces, which have been invoked to get rid of the resultant force, pass through the intersection of the planes and so give no moment. Consider an element dr on the lower surface of the right-hand plane, where ϕ lies between α and $-\beta$; its contribution to the torque, in the positive direction, is

$$-\tfrac{1}{2}\rho q^2 r\,dr$$
$$= -2\mathrm{A}^2\rho q_0^2 \sin^2(\phi-\gamma)(\cos\phi-\cos\alpha)d\phi/(\sin\phi+\sin\beta).$$

The disappearance of the index k, except in so far as it is involved in $\sin\beta = k\sin\alpha$, is rather surprising here, and makes it possible to integrate the expression.

It will be noticed that the formula for the element of torque gives the correct sign throughout the entire range of ϕ from $-\pi$ to π.

$$\text{It is}\quad \begin{array}{lll} + & \text{for} & -\pi<\phi<-(\pi-\beta) \\ - & ,, & -(\pi-\beta)<\phi<-\alpha \\ + & ,, & -\alpha<\phi<-\beta \\ - & ,, & -\beta<\phi<\alpha \\ + & ,, & \alpha<\phi<\pi, \end{array}$$

in each case opposite to the sense of the moment of the pressure on the corresponding part of the planes

Evaluation of the indefinite integral gives

$$2\int \sin^2(\phi-\gamma)(\cos\phi-\cos\alpha)d\phi/(\sin\phi+\sin\beta)$$
$$= -(\cos 2\beta\sin 2\gamma - 2\cos\alpha\sin\beta\cos 2\gamma)\phi$$
$$+2(\cos\alpha\sin 2\gamma - \sin\beta\cos 2\gamma)\sin\phi$$
$$+\cos 2\gamma\sin^2\phi + 2(\sin\beta\sin 2\gamma$$
$$+\cos\alpha\cos 2\gamma)\cos\phi - \sin 2\gamma\sin\phi\cos\phi$$
$$+2\sec\beta\{(\cos\beta-\cos\alpha)\sin^2(\beta+\gamma)\log\sin\tfrac{1}{2}(\phi+\beta)$$
$$+(\cos\beta+\cos\alpha)\sin^2(\beta-\gamma)\log\cos\tfrac{1}{2}(\phi-\beta)\}.$$

When the range of integration includes one of the edges $\phi=-\beta$, $\phi=-(\pi-\beta)$, there is physical justification for taking the principal value of the improper integral.

For the two planes taken together, with limits $\pm\pi$, the torque is

$$2\pi\mathrm{A}^2\rho q_0^2(\cos 2\beta\sin 2\gamma - k\sin 2\alpha\cos 2\gamma)$$

with positive sense, *i.e.* counter-clockwise.

When the two planes are flattened out into one, $k=0$, $\beta=0$, the breadth $=4\mathrm{A}$ and the moment $=2\pi\mathrm{A}^2\rho q_0^2\sin 2\gamma$. This agrees with the known result for the case of an elliptic cylinder reduced to a lamina, viz., $\tfrac{1}{8}\pi\rho q_0^2 c^2\sin 2\gamma$.

It will be seen that the torque in every case varies with the angular position of the planes in the usual "quadrantal" manner, the amplitude, or maximum value being

$$2\pi A^2\rho q_0^2(\cos^2 2\beta + k^2 \sin^2 2\alpha)^{\frac{1}{2}}$$
$$=2\pi A^2\rho q_0^2\{1-4k^2(1-k^2)\sin^4\alpha\}^{\frac{1}{2}}.$$

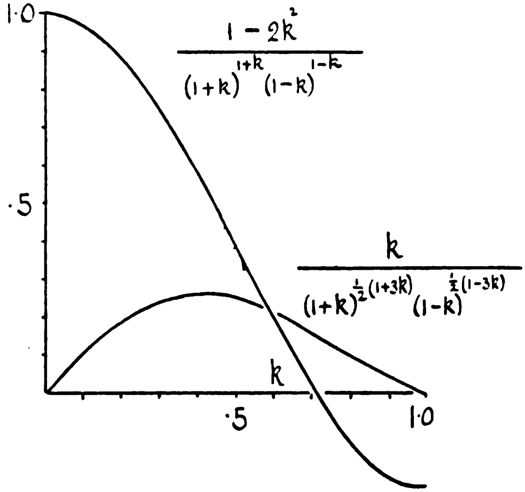
In general A, α are complicated functions of the dimensions of the planes together with the angle $k\pi$. Explicit formulæ can be got when the breadths are equal, for then $\alpha=\frac{1}{2}\pi$, $\beta=\sin^{-1}k$, γ is the inclination of the stream to the exterior bisector of the angle, the breadth of either plane is

$$2A(1+k)^{\frac{1}{2}(1+k)}\,.\,(1-k)^{\frac{1}{2}(1-k)}=a, \text{ say,}$$

and the torque is

$$2\pi A^2\rho q_0^2(1-2k^2)\sin 2\gamma$$
$$=\tfrac{1}{2}\pi a^2\rho q_0^2 \sin 2\gamma\,.\,(1-2k^2)/(1+k)^{1+k}(1-k)^{1-k}.$$

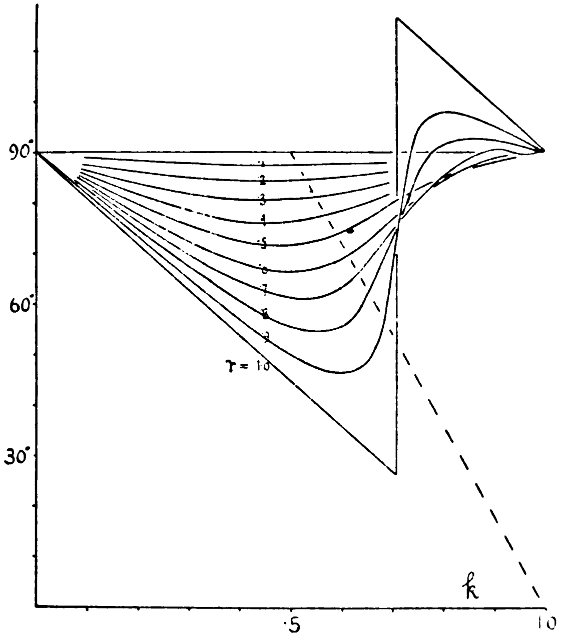
Fig. 3.



The course of the function of k is shown on fig. 3, which therefore gives the variation of the maximum couple for equal planes of given dimensions as the angle between them is changed. The torque vanishes for the symmetrical positions

$\gamma=0$ and $\gamma=\frac{1}{2}\pi$, the planes are then in equilibrium relative to the stream. Examination of the sense of the couple shows that the equilibrium is stable when the direction of the stream coincides with the interior bisector of the angle, for $k<\frac{1}{\sqrt{2}}$, with the exterior bisector for $k>\frac{1}{\sqrt{2}}$. This illustrates the general tendency of a body to set its long dimension across the stream. Evidently, as the planes are shut up together from a wide-spread angle, we must pass from one configuration to the other. The critical form is reached

Fig. 4.



when the planes make an acute angle of about 52°·8. The planes will then remain indifferently in any posture relative to the stream. It is only when the planes are equal that this curious state of affairs is found. With unequal breadths there is always one definite position of stable relative equilibrium in the stream, with an unstable position at right angles to it.

The way in which this position varies with the inclination of the planes and the ratio of their breadths is shown on fig. 4. It is more convenient, in discussing the matter, to regard the planes as moving steadily through a quiescent liquid. Each curve on the figure refers to a definite breadth ratio, from 0·1 to unity. The abscissa is the exterior angle between the planes, $k\pi$, while the ordinate is the inclination to the larger plane of the stable direction of steady translation through the liquid, viz. $(\frac{1}{2}\pi - k\alpha + \gamma)$, where γ is taken as acute. To obtain these curves another set was first plotted in which each curve corresponded to a given value of k, and the direction of motion was plotted against the breadth-ratio for a succession of values of the angle α. From these the direction-angle was then read off at the points where the ordinate corresponding to any breadth-ratio crosses the series of curves, and so the material for fig. 4 was obtained.

The straight-line graph shows the case of equal planes with the sudden change from the internal to the external bisector at external angle $\pi/\sqrt{2}$. When the length of one plane is slightly decreased this discontinuity passes into a very rapid change of orientation in the neighbourhood of the same angle. With still smaller lengths of the second plane the graph ceases to rise above the 90° level. If we begin with the two planes in line ($k=0$), and rotate the smaller plane, the direction of steady translation first rotates in the same direction and then returns to the normal position. There are two special cases of some interest :

(1) The points where the curves are met by the broken line whose ordinate is $(1-k)\pi$ correspond to stable translation in the direction of the shorter plane. It will be seen that this is possible for any breadth-ratio.

(2) If the curve for an assigned ratio intersects the level of 90° there is steady translation in the direction normal to the larger plane, just as if the other were not attached. We have then $\gamma = k\alpha$, and the equation connecting k and α becomes

$$k \sin 2\alpha - \tan 2k\alpha (1 - 2k^2 \sin^2 \alpha) = 0.$$

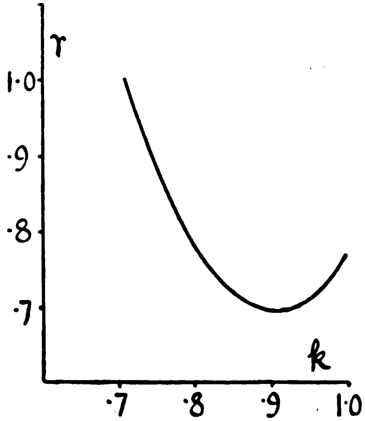
The assumed motion occurs when this equation for k has a root between 0 and 1. For $\alpha < \frac{1}{4}\pi$ the left-hand side is negative and finite throughout the range. For $\alpha > \frac{1}{4}\pi$ it changes sign through infinity from negative to positive at $k = \pi/4\alpha$. There will be a root between this value and $k=1$ provided the differential of the expression with respect to k

is positive at $k=1$, *i.e.*, if

$$\sec 2\alpha(4\sin 2\alpha - \sin 4\alpha - 4\alpha) > 0.$$

The expression in brackets vanishes for $\alpha = 61^{\circ}\cdot 3$ approximately. For this value of α the third root coincides with $k=1$, and as α increases to 90° the root moves back to $1\sqrt{2} = \cdot 707$. The corresponding values of the breadth-ratio, r, are ·77 and unity, but r does not increase continuously from the former to the latter value as the associated values (αk) move continuously from $(61^{\circ}\cdot 3, 1)$ to $(90^{\circ}, \cdot 707)$. The complicated nature of the connexions between r, k, α, makes it necessary to examine the matter arithmetically. When this is done it is found that r sinks to a minimum of about ·69 for $\alpha = 67^{\circ}$, $r = \cdot 91$, approximately. The connexion between k and r is shown on fig. 5.

Fig. 5.



We can now describe the course followed by the curves of fig. 4 at their right-hand ends. The curve for $r = \cdot 69$ is bent upwards to touch the lower side of the 90° level at about $k = \cdot 91$. Curves for higher values break through this level, there being two intersections up to $r = \cdot 77$ and one for r between ·77 and unity. This means that for breadth-ratios between ·69 and ·77 there are two inclinations of the planes which give steady translation perpendicular to the larger plane, above ·77 there is one inclination, and below ·69 none.

The scheme of a broad plane, moving in its own direction, with a short plane attached to it at an angle, suggests a simplified model of a ship and rudder. It is perhaps worth while to point out the complete lack of similarity in the actions in the two cases. If in our ideal case we began with the two planes in line and moving with unstable steady motion in their own direction, a slight deflexion of the rudder-plane will cause the whole to swing into the stable direction, nearly perpendicular to the large plane. The turning will be through the acute angle, and this is in the direction opposite to that in which a rudder turns a ship. Further, the torque will be in the same direction whether the motion is ahead or astern.

An expression can be found for the torque at any angle when the rudder-plane is a small fraction of the breadth of the other, in this case the parameter α is small, $\beta = k\alpha$, and γ is also $= k\alpha$ when the motion is along the larger plane, for then

$$-\gamma - k(\tfrac{1}{2}\pi - \alpha) = -\tfrac{1}{2}k\pi.$$

We find the following approximations :

Breadth of large plane $= 4\,\mathrm{A} = a$ say.

Breadth of small plane $= \mathrm{A}(1+k)^{1+k}(1-k)^{1+k}\alpha^2 = b.$

Torque $= \mathrm{A}^2\rho q_0{}^2\tfrac{4}{3}\pi k(1-k^2)\alpha^3.$

Eliminating A, α we find the torque

$$= \tfrac{2}{3}\pi\rho q_0{}^2 a^{\frac{1}{2}} b^{\frac{3}{2}} . \, k/(1+k)^{\frac{1}{2}(1+3k)} . \, (1-k)^{\frac{1}{2}(1-3k)}.$$

This function of k is plotted on fig. 3.

It remains to try the effect of superposing a circulation on the simple flow discussed in the present paper, on the lines which have, in the hands of Prandtl and others, led to important developments in the theory of the aeroplane.

LXXXII. *Alternative Currents in Rarefied Oxygen in the same Circuit.* *By* Rev. P. J. KIRKBY, *D.Sc.*[*]

Introduction.

1. IN 'Nature,' Aug. 19th, 1922, I gave a preliminary account of certain peculiar effects in the electric discharge of oxygen. They were observed in the course of a further investigation into the nature of those discontinuities in the electric discharge through oxygen at pressures close to ·8 mm., about which I published an account in the Philosophical Magazine of April 1908. The latter effects were exhibited in that region of a long cylindrical discharge which is known as the positive column.

The positive column in oxygen at pressures of the order ·8 mm., with which these researches are chiefly concerned, occupies the whole length of the discharge with the exception of the first five to eight cm. from the cathode (or negative electrode). Thus in a discharge-tube where the electrodes are 20 cm. apart, the column appears as a uniform pale pink cylinder, about 13 cm. long at the pressure ·8 mm., terminating at the anode or positive electrode. In oxygen striæ, which in other gases present such a striking appearance, do not often appear, at least at our pressures: when they did, they were close together and entirely unlike those of other gases.

2. Within this luminous positive column the *electric force* (fall of voltage per cm.) along the length of the tube is constant; and it is here that the discontinuities described in the Phil. Mag. of Feb. 1908 were observed. They were of the following nature:—As the pressure was raised from ·53 to ·8 mm., it was found that the electric force rose with perfect regularity in arithmetical progression with equal increments of pressure from 14·4 to 21·4 volts per cm.; after which an imperceptible increase of pressure brought about a radical change in the discharge, so that the electric force within the positive column was reduced to about 11 volts per cm. Moreover, this discontinuity was a reversible effect: namely, a very slight decrease of pressure caused the electric force to jump back to about 20 volts per cm., indicating the recovery of the previous state of the discharge. It should be added that when the pressure was increased beyond the discontinuity value of about ·8 mm., the same force was observed

---

[*] Communicated by the Author.

to *decrease* rapidly to a minimum of about 4·5 volts per cm. (at a pressure between 1·5 and 2 mm.), after which it increased with the pressure.

3. The experiments to be described in this paper show that the reversible effect just alluded to, produced by an imperceptible change of pressure, can be produced without any change of pressure, and not merely at one definite pressure, but at any pressure within a certain region of pressure, of which ·8 mm. is about the centre. Thus if the pressure of oxygen in a discharge-tube, *forming part of a fixed circuit*, falls within that region of pressure (so far observed to be ·54 to 1·04 mm.) two different discharges are producible, one characterized by a positive column with high electric force, the other characterized chiefly by a positive column of much smaller electric force.

Ordinary and Extraordinary Currents defined.

4. Since it is necessary frequently to distinguish between these two types of current, I propose to call the former of these alternative discharges, namely the one with the high electric force in its positive column, the *ordinary current* (or discharge, etc.), and the other the *extraordinary current*, borrowing these adjectives from the terminology of double refraction. For the ordinary currents are very regular: they are analogous to currents of similar magnitude and at similar pressures through hydrogen and nitrogen, having electric forces in their positive columns of the same order of magnitude with those gases. (See section 18.) And on the other hand, the extraordinary discharges appear to be *sui generis*.

5. In addition to having an abnormally small force in its positive column the extraordinary current in a given circuit is distinguished from the ordinary by its greater value, and also by its positive column being somewhat longer (about 1 cm.) than that of the ordinary, and also somewhat paler in colour.

Further, in contrast with the ordinary current, the extraordinary has a tendency to disturbance by the passage of electricity, being perhaps more sensitive to the presence of ozone. Thus if the discharge is made to alternate several times between the ordinary and extraordinary currents, the latter will exhibit a slight progressive modification, while the ordinary will remain unchanged.

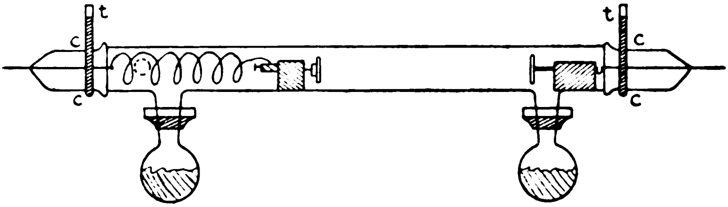
The Experiments.

6. The experiments consisted in passing a steady current through a discharge-tube between two circular electrodes, of which the anode was movable so that the length of the discharge could be varied. The current came from a battery of small accumulators of 1020 volts or less, and passed through a high resistance which could be varied up to two megohms. By this means it was possible to study currents of various length and magnitude and to determine their electric forces in the positive column.

The Discharge-tube.

7. This is shown in elevation (projection on a vertical plane through the tube's axis), and drawn to scale, in fig. 1. A cylindrical tube of nearly 48·5 cm. length and 2·8 cm. internal diameter (3·1 external diam.) was closed at both ends by airtight glass caps, through which protruded thick platinum wires fused to them. The platinum wires were attached to stiff silver wires passing through the interior of the caps, and connected by thin wires to the electrodes.

Fig. 1.



The caps were designed to make a perfectly gas-tight fit to the ends of the glass tube, which was slightly inclined as each end to receive them. A narrow side-tube (*t*, fig. 1) was fused to each cap, and a small circular protuberance, containing the base of this tube, was blown round the cap, forming with the outer surface of the discharge-tube, with the cap fitted on, a little circular canal (*c*, *c*), into which the side-tube opened. The internal surface of each cap on both sides of the circular canal was ground to fit its end of the discharge-tube, which was also ground. By using vaseline optical contact was then secured between the caps and the tube; and mercury was poured into the side-tube (*t*), filling the canal and part of the side-tube itself (as shown in fig. 1).

The side-tubes being vertical and about 4 cm. high, when they were more or less full of mercury the mercury within the canals had everywhere a pressure greater than atmospheric pressure, and was therefore able to stop any air that would have been otherwise forced by the pressure of the atmosphere between the tube and the cap.

By this means, notwithstanding the large extent of the surfaces of contact exposed to possible air-leaks, not the slightest leak was ever observed through the discharge-tube, even after weeks at a time, though a leak of less than ·001 mm. was detectable by the particular form of McLeod gauge that I employed. The caps could be taken off without letting mercury into the apparatus by inverting them, to allow the mercury to run out of the canals, before taking them off.

The small bulbs below the tube in fig. 1 are drying vessels containing phosphorus pentoxide, about 5 cm. in diameter. They were ground to fit the small vertical tubes blown into the main discharge-tube, and carried mercury cups, thus obviating any air-leak. This apparatus was made to my design by Messrs. J. J. Griffin, Kingsway, London.

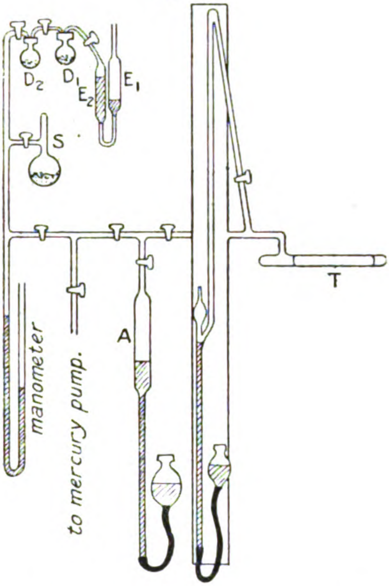
Electrodes.

8. The electrodes were made of pure gold ·25 mm. thick, backed by pure silver ·75 mm. thick, to exclude oxidation. They were fixed to small solid iron carriers, capable of sliding along the discharge-tube, and connected by fine wires to the silver continuations of the platinum wires which protruded through the glass caps. By means of an electromagnet outside the discharge-tube the electrodes could thus be moved along it into any desired position. The cathode only needed slight adjustments. But the anode was connected to the negative terminal by a long thin coiled copper wire; and later on by a thin brass wire. As the anode was moved back by the electromagnet, the thin wire coiled itself behind it, so that it was easy to adjust the anode to any distance from the cathode. The diameter of the anode was 2 cm. That of the cathode was at first 2·4 cm.; but after a number of experiments one of the caps was accidentally broken and the opportunity was taken to replace the cathode by a similar one of 2·75 cm. diameter, which fitted the tube closely in the reconstructed apparatus. These pure gold and silver electrodes were supplied by Messrs. Matthey and Johnson.

Preparation of the Oxygen for the Experiments.

9. The scheme of the whole apparatus is sufficiently indicated by the diagram of fig, 2. The oxygen was produced by electrolysis of sodium hydrate in the tube E_2. The tube E_1 opens into the air through a tube (not shown in the figure) full of powdered caustic potash, to prevent any carbon dioxide from entering into the electrolyte as the air is drawn into E_1. The oxygen was dried in D_1, D_2 over phosphorus pentoxide, and passed into the reservoir S, containing the same substance, from which it passed into the

Fig. 2.



discharge-tube T, the McLeod gauge, and the vessel A. A had a capacity commensurate with that of the discharge-tube and McLeod gauge together. Its long barrel was provided with a scale, so that by raising or lowering the mercury by the necessary amount, the proper taps open, the pressure in T could be adjusted accurately. It was also easy by means of this barrel, its cross-section known, to ascertain the joint capacity of T and the McLeod gauge.

All the connexions of the apparatus were of fused glass. No rubber was used except for working the mercury pump, A, and the McLeod gauge; and the lower junction of the rubber with the glass on this gauge was in a glass full of mercury. All the taps had mercury cups.

The whole of the apparatus, with all the taps open, was then exhausted to a low pressure and thoroughly tested for airtightness, and the electrolyte in E_2 was drawn up to the tap before the generation of oxygen. These precautions guaranteed the oxygen to be of a high degree of purity. It entered the discharge-tube by a horizontal side-tube blown into the former, as indicated by the little dotted circle of fig. 1, near the left cap.

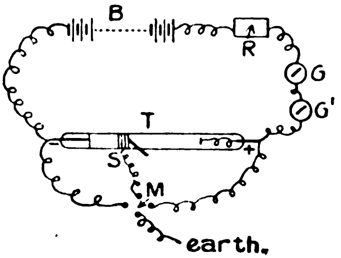
Method of Experiment.

10. The method eventually used for examining the alternative discharges producible in the discharge-tube, without any alteration in the electric circuit containing it or in the mass of the oxygen in that tube, was as follows :—

A strip of tinfoil of about 3 cm. width was wrapped round the discharge-tube, forming a short cylinder. It was placed at such a distance from the cathode that the positive column just about entered the cylinder. If now this ring, or little cylinder, is connected with the anode, the larger or extraordinary current will pass in general, and will continue if the ring is insulated. But if the ring is connected to the cathode, the smaller or ordinary current will pass and will continue after insulating the ring.

This ring of tinfoil was subsequently replaced by a ring, S, consisting of four turns of fairly thick copper wire, bent round the discharge-tube and in contact with it, so as to have a width of about one cm. It was attached to a vulcanite handle, by which it could be moved to any required position on the tube.

Fig. 3.



11. Figure 3 shows the electrical arrangements. The battery B maintained a steady current, determined by the resistance R, through the discharge-tube T. G was a high

resistance voltmeter (36,240 ohms) used as a galvanometer, capable of measuring currents exceeding ·2 milliampere, and G′ a still more sensitive one, which confirmed the smallest readings of G. M is a block of paraffin, having four small holes filled with mercury, by which the ring S could be immediately earthed or connected with anode or cathode. This method was used as the simplest way of charging the ring S positive or negative to an adequate potential. The circuit was well insulated for the purpose in view.

Determination of the Electric Force in the Positive Column.

12. The uniform electric force in the positive column was determined by a method which I have often used in other * researches, and which is free from the serious objection to the use of exploring wires in the discharge that they disturb the natural electrostatic field of the discharge.

The electrodes being at a distance D apart, a current C is passed from a battery B through a resistance R (one or two megohms), adjusted to give a suitable value to C. The anode is then moved through a distance d cm. nearer the cathode and B is reduced to $B-b$, R being unchanged and b being such that the current C is unchanged. Then the electric force is b/d volts per cm., provided that the two discharges are long enough to have positive columns. The validity of this method is easily proved by the constancy of b/d, when B, R, C remain constant. In practice it is difficult to hit exactly on b, the number of volts by which to reduce the battery so as to reproduce the previous current C when the anode has been moved through the distance d towards the cathode. And it is not necessary. For it is easy to obtain two adjacent values of b giving currents slightly greater and less than C, and then by interpolation to determine b precisely. The errors inherent in this method are a small percentage, unless the force in the positive column is small, in which case the errors are greater. Usually I took d to be about 1 cm. less than the length of the positive column; and having determined the electric force therein, I confirmed the result by a second observation in which d was half its previous value.

Another method, depending on the fact that the potential difference of the electrodes is practically independent of the current provided the range of variation of the current is restricted, is used below. (Sections 34 ff.)

---

* P. J. Kirkby, Phil. Mag. March 1907, April 1908; Proc. Roy. Soc. A, lxxxv. p. 151.

Preliminary Tables.

13. Before dealing with the experiments which exhibit the alternative discharges through oxygen with a fixed circuit, I give some tables which will illustrate the great difference of the electric forces in the positive columns of the two types of current, the ordinary and the extraordinary, and the abrupt transition which the discharge makes, when it is not controlled, at a certain critical pressure, which is not absolutely fixed but depends on the magnitude of the current and the condition of the gas, lying within, or adjacent to, the range of pressure ·6 to ·8 mm.

The values of Y in Table I. were obtained from many different masses of oxygen by the method described above, at the pressure and with the current (to the left of the Y) stated on the same line. The current was not controlled: whether it was the ordinary or the extraordinary was a matter of self-determination. It is, however, easy to distinguish the ordinary from the extraordinary by the greater value of Y, characteristic of the former, at the same or neighbouring pressures.

14. The table exhibits the currents at pressures of ·67 mm. and below as ordinary, and currents at pressures of ·9 mm. and above as extraordinary. At pressures between these figures, the nature of the current depends on its magnitude: the smaller the current, the higher the pressure at which it appears spontaneously as ordinary, and *vice versa.*

To save space and to facilitate comparison between the Y's of currents which differ by a substantial fraction of a milliampere, the results are given in three double columns, which contain currents of about the same magnitude, namely, within 20 per cent. of ·25 m.a., of ·47 m.a., and of 1·25 m.a., respectively. This is indicated at the head of each double column.

A comparison of the values of Y in the second and third double column, at the pressures ·48, ·34, ·23 mm., indicates that an increase of ·74 m.a. in the current goes with a *decrease* in Y of 1·2 volts/cm. If, then, we assume that Herz's well-known rule * for similar discharges in nitrogen and hydrogen, namely, that in a given tube the concomitant increase in current and decrease in Y are in a constant ratio —if we assume that such a rule applies to the *ordinary* discharges of oxygen, we may conclude that the correction to be applied to the Y of any current C of these orders of magnitude, in order to get the Y of a smaller current, $c-c$, m.a., is plus 1·6 c volts per cm. (The corresponding correction for nitrogen discharges in our tube would be just twice as much.)

---

* Herz, *Wied. Ann.* liv. p. 244 (1895), or, Sir J. J. Thomson, 'Conduction of Electricity through Gases,' 1903, p. 456.

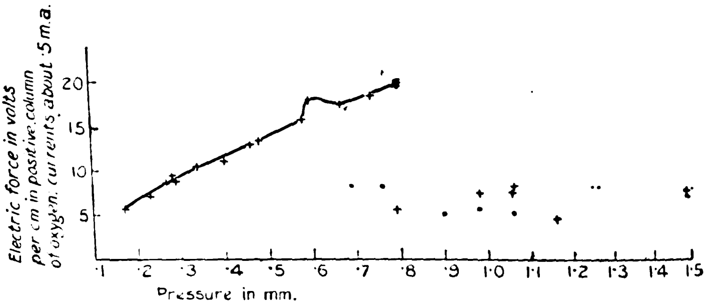
TABLE I.

p = the pressure of oxygen in mm.
C = the current in milliamperes.
Y = electric force in the positive column in volts per cm.

	C > ·2 m.a. < ·31 „		C > ·38 m.a. < ·57 „		C > 1·1 m.a. < 1·43 „	
p.	C	Y	C	Y	C	Y
1·49	...	...	·5	7·8	1·4	7·3
1·16	...	...	·54	4·6		
1·06	...	...	·495	8·1	1·36	5·25
1·06	...	...	·525	7·6	1·39	5·15
·98	...	...	·47	7·5	1·41	5·8
·9	...	...	...	...	1·43	5·0
·81	·201	20				
·81	·256	20·3				
·79	...	...	·57	5·7		
·78	·304	19·5				
·76	...	...	...	...	1·33	8·2
·74	...	...	·414	18·6		
·69	...	...	...	...	1·3	8·3
·67	...	...	·382	17·6		
·6	·216	18·8	·42	18·0		
·58	...	...	·5	15·8		
·57	...	...	...	...	1·1	13·3
·48	...	...	·45	13·4	1·16	12·0
·46	·218	13·6				
·46	·25	14·4	·47	13·0		
·4	·256	11·4	·47	11·1		
·34	...	...	·495	10·6	1·23	9·4
·29	...	...	·495	9·0		
·28	·267	10·1	·48	9·5		
·27	·247	10·3	·453	8·7	1·06	8·3
·23	...	...	·52	7·0	1·29	5·8
·16	...	...	·47	5·3		

This result is in agreement with Table I. For if we plot the Y's of the ordinary currents in the second double column of that table against the pressures, the points determine a locus, the slight difference between the various currents in that double column and their mean, ·47, producing an imperceptible effect in the corresponding Y's. This is shown in fig. 4, in which the points thus determined are shown by a cross. It is also clear that the points whose coordinates are p, Y, from the first double column of Table I., fall very nearly on the locus of fig. 4, and that the slight correction of 1·6 c, mentioned above, though not so insignificant as before, improves the approximation. But I have not complicated the figure of the locus by adding points from the other columns, except one (the star, $p = ·81$, $Y = 20$) from the first double column.

Fig. 4.



15. A curious feature of the locus is produced by the value of Y = 18, at the pressure ·6. If this is suppressed, the locus is a smooth curve (of continuous curvature). But I have found it impossible to do this, and to regard it condemned, as exceptionally erroneous, by the other observations, because no result seems more repeatedly confirmed. (See Table V.) It seems therefore necessary to conclude that there is a singularity here in the locus, the electric force making a sudden increase in value, after which it remains more or less constant while the pressure rises to about ·74. If this is so, it is obviously connected with the exceptionally unstable nature of the oxygen in the immediate neighbourhood of this pressure.

The ordinary discharges appear thus to be as congruent among themselves in respect of their positive columns as the discharge of other gases. The values of the electric force in those columns are determinate and easily repeatable. Apart from the seeming anomaly alluded to above, their only distinguishing feature is the big rate of increase of the force per mm. rise of pressure, the current being constant. This quantity, dY/dp, the slope of the curve of fig. 4, is, *e. g.* 70 per cent. greater than that of a similar curve for hydrogen.

16. The extraordinary discharges, on the other hand, have positive columns of very different characteristics. For not only is the electric force of a different degree of magnitude, but the discrepancies in their values cannot be accounted for by errors of observation. There is evidently a disturbing factor, which makes it difficult to reproduce an extraordinary current with the same precision which characterizes the ordinary. This fortuitous element will be discussed later.

The electric forces in the extraordinary positive columns, given in Table I., are represented in fig. 4 by isolated points, marked by crosses or dots according as the force is to be found in the second or the third double column. All these values of Y fall within the parallel lines,

$$Y = 6{\cdot}4 \pm 2.$$

There is thus no locus, but a tendency towards a value more or less constant in this range of pressure. This mean value of Y is 6·4 volts per cm.

17. The values of the ordinary Y's in Table I. are in agreement with those given in my first paper (Phil. Mag., April 1908), although the latter were obtained with a constant current of 2·5 milliamperes. If the two discharge-tubes had been equal in diameter, having regard to the correction inferred above (1·6 *c*), we should expect Y in Table I. to be 3·4 volts per cm. greater than the corresponding value of the first paper, and not equal to it. But the present discharge-tube was 2·8 cm. in diameter as against the 2·4 of the first discharge-tube, so that the effect of the increased diameter appears approximately to balance the effect of the diminished currents on the electric force. There are no data for deducing the effect of the diameter of the tube on Y in oxygen; but if it is about the same as in nitrogen, the difference between the diameters of the two tubes would produce just about the difference in corresponding Y's necessary to balance the 3 or 4 volts per cm. attributable to the difference of current. (See Herz's figures, *loc. cit.*)

Oxygen Discharges contrasted with Hydrogen Discharges.

18. In order to illustrate the anomalies of oxygen in this range of pressure by contrast with the behaviour of an ordinary gas, a series of determinations of the electric force in positive columns of hydrogen were made by the same

method and in the same apparatus and over the same range of pressure. The results are given in Table II.

TABLE II.

Hydrogen (p, Y, C as in Table I.).

p.	Y.	C.
1·35 ……	26·7	·364
1·14 ……	23·2	·215
1·14 ……	20·7	·42
·85 ……	19	·238
·82 ……	17·3	·458
	18·8	·255
·66 ……	16·3	·258
·66 ……	14·5	·466
·58 ……	16·0	·121
·51 ……	14·5	·143
·29 ……	11·1	·072
·28 ……	11·6	·095
·24 ……	11·9	·057

Here $Y=13p+8·4$, except for the currents greater than ·4.

If we omit the Y's of the three currents greater than ·4 (which, in view of what has been said above, will have electric forces sensibly less than would correspond to the mean of the other currents), the table, with the exception of one value of Y ($p=·29$), is represented by the equation

$$Y = 13p+8·4,$$

within an error of 4 per cent.; which is thus the equation for currents adjacent to ·2 milliampere for the range of pressure ·24 to 1·35 mm.

If this line is drawn on fig. 4 it passes across the curve at a smaller slope, dY/dp, to the axis of pressure than that of the curve drawn in that figure. Nor is there any suggestion of discontinuity or arrest about it, though the values of Y corresponding to the same pressure are, up to the pressure ·8, of very similar magnitude.

The big increase of electric force in the positive column per unit increase of pressure (current constant) is (as observed above, section 15) a characteristic of the ordinary discharges in oxygen at pressures where transition of current from ordinary to extraordinary takes place. In my first paper I gave the equation

$$Y = 25·6\,p+·9$$

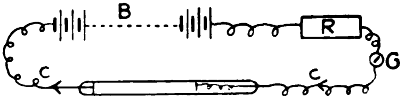
for the constant current 2·5 m.a. and for pressures between ·5 and ·8 mm. in the tube of 2·4 mm. diameter. In this case the gradient dY/dp is 25·6, and the gradient of the curve of fig. 4 is, though less, of similar magnitude. The result of this fact is that small errors in the determination of the pressure may introduce serious ones into the values of Y. For instance, an error of ·05 mm. would introduce an error of more than 1 volt per cm. in Y. This is to be borne in mind in estimating errors of observation, especially when it is necessary to compare values of Y determined with different McLeod gauges, the constants of which involve errors of determination, which might jointly produce discrepancies exceeding ·05 mm. in the determinations of the same pressure.

Anomalies of Oxygen further illustrated.

19. The simplest way of illustrating the anomalies of oxygen and the sharp discontinuities that appear in the positive columns when the pressure is near the value ·7 mm., is perhaps to plot the voltage-difference of the electrodes against the pressure when the latter alone is made to vary in an otherwise constant circuit of which the discharge-tube is part.

If the circuit consists simply of a constant battery B, a constant resistance R, a galvanometer G, and the discharge-tube T with its electrodes a fixed distance, D, apart as in fig. 5; then, if D is great enough to permit an adequate positive column, the current C will undergo a sharp discontinuity at a certain (somewhat fluid) critical pressure in the neighbourhood of ·7 mm.

Fig. 5.



Now the current is connected with the electrodal potential difference by the linear equation,

$$X = B - CR,$$

so that the pressure-current curve is the orthogonal projection of the p–X curve. In particular, if R is a megohm and C is measured in microamperes and the battery is 1000 volts, the curves p–C, p–X are symmetrical with respect to the line parallel to the axis of p and distant 500 from it. One curve is the optical image of the other in this line. Such was roughly the state of things during the experiments recorded in Table III., D being 19·7. Hence it is sufficient to draw the p–X curve for the purpose of illustration: the p–C curve looks practically the same but inverted. The exact details are given at the head of the table.

TABLE III.

Showing the variation of the voltage-difference X of the electrodes, and also of the electric current, C m.a., as the pressure varies up to 1·09 mm., with a constant circuit. Battery 1014 volts, and distance between electrodes 19·7 cm. Total ohmic resistance of circuit, galvanometer included, ·923 megohm.

p.	X.	C.	p.	X.	C.
1·09	498	·557	·66	524	·550
·89	502	·555	·65	606	·442
·79	510	·544	·60	602	·447
·66	622	·425	·54	584	·467
·75	498	·557	·50	576	·475
·71	504	·550	·40	560	·492
·68	504	·550	·38	560	·492
·67	504	·550	·32	552	·500
·66	504	·550	·27	551	·502

20. That the discontinuities exhibited in Table III. are due to the positive column is proved by Table IV., which applies to a fixed circuit as before (illustrated in fig. 5), with the difference that the influence of the positive column was practically removed by fixing the electrodes at the distance 7·9 cm. At the pressure ·29 the positive column was observed to begin 8 cm. away from the cathode. (Here the electric force was 9·2 volts per cm.) Hence the positive column in the case of all the experiments recorded in Table IV. was very short, and its effect on the discharge so slight as to obliterate the discontinuities which make their appearance with longer positive columns.

21. If the voltage-differences of the electrodes, X, in Table III. are plotted against the pressures, the greater values of X, namely those of the ordinary currents, which we call X_0 (section 24), determine a curve. This is shown very clearly in fig. 6, where the little crosses (or rather, their centres) are the points whose coordinates are corresponding

TABLE IV.

Showing the substantial constancy of the voltage-difference X of the electrodes, and also of the current C (m.a.), as the pressure *p* varies up to 1·12 mm., with a fixed circuit and little or no positive column. Battery 946 volts, D=7·9 cm. Total ohmic resistance of circuit ·923 megohms.

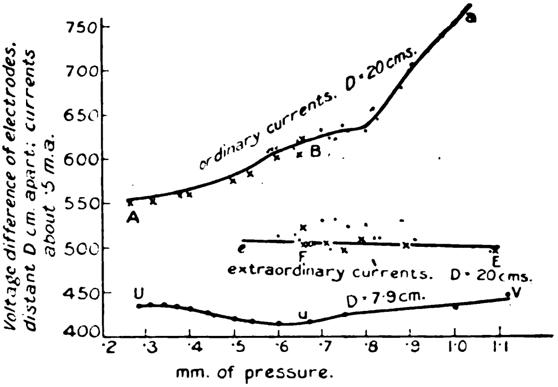
p.	X.	C.
1·12	446	·54
1·0	433	·555
·75	426	·563
·67	418	·575
·6	413	·577
·54	417	·575
·5	420	·57
·49	420	·57
·44	426	·56
·4	431	·56
·37	433	·555
·34	436	·552
·31	436	·55
·284	436	·55

values of *p* and X in Table III. These apply to discharges in which the distance D between the electrodes is 19·7 cm., and those between A and B clearly determine a locus. The curve AB has been drawn slightly above that locus, and is the corresponding locus for D=20 cm. (The necessary correction is scarcely perceptible, being an addition to the ordinate X at any pressure of ·3 Y, where Y is as usual the electric force in the positive column of the discharge and is given by the curve in fig. 4.) It will be shown below that the whole curve AB*a* is definitely determined by many other observations in addition to those of Table III., as the mean locus of the points p, X_0 when D=20 cm., for pressures up to about 1 mm., and currents of similar magnitude to ·5 m.a., for which X_0 is practically independent of the current. (See section 27.)

The other values of X in Table III., namely the smaller ones which apply to extraordinary discharges, determine (with the exception of one) the straight line FE in fig. 6. But other determinations of X during the passage of extraordinary currents are by no means equally accordant to this result; for, as already noticed in sections 4 and 16, such currents are, unlike ordinary discharges, peculiarly susceptible to certain effects producible by the passage of electricity.

Table IV. similarly determines, and with precision, the curve U*u*V, which practically contains all the points plotted on fig. 6 to represent the observations of that table. This curve will be discussed later.

Fig. 6.



22. The results so far described were obtained with self-determined discharges, which appeared as ordinary or extraordinary currents according to the pressure or magnitude. The following is an account of alternative currents through oxygen obtained without varying the pressure or the circuit.

Alternative Currents in a Discharge-tube of Oxygen in a given Circuit.

It is simplest to start with a detailed description of a selection of the experiments carried out in the manner described in sections 10 and 11 above with the arrangements illustrated in fig. 3. The notation and abbreviations used are given in section 24.

(i.) The ring of tinfoil, S, 3 cm. broad, fitting the discharge-tube with its edges at the distance 3 and 6 cm. from the cathode, the anode being 19·7 cm. from the cathode, and the pressure ·84 mm., it was found that, when S was connected with the anode, the current was ·47 m.a., which persisted when S was insulated, but changed at once to ·33 m.a. on connecting S to the cathode, and so remained on insulating S. The change in E.P.D. (potential difference of electrodes) was from 555 to 683 volts.

(ii.) At the same pressure ·84 mm. and the same distance, 19·7 cm., between the electrodes, but with the edges of S 2 and 5 cm. from the cathode, the current changed in the manner described in (i.) from 1·21 m.a. (E.P.D. 551 volts) to ·965 m.a. (E.P.D. 641), and from ·47 m.a. (E P.E. 558) to ·331 m.a. (E.P.D. 687), and from ·442 (E.P.D. 584) to ·331 m.a. (E.P.D. 687).

The positive column was observed to begin 7 cm. from the cathode when the current 1·21 m.a. was passing, and 8 cm. from it during the discharge ·965 m.a.

Further, the alternative currents 1·21 and ·965 m.a. were easily made to alternate backwards and forwards by connecting the strip S to anode or cathode respectively (after which S could be insulated without affecting the current). But the smaller currents were not easily reversible. Finally the gas tended to lose this reversibility. (It is natural to attribute this to the loss of purity in the oxygen through the generation of ozone, as suggested by the slight observed decrease of pressure.)

(iii.) The copper ring, mentioned above, S (fig. 3), now replaced the tinfoil ring, just embracing the end of the positive column. With $D=21·8$ cm., $B=990$ volts, $p=$ ·76 mm., the current was made to alternate between 1·186 and ·883 m.a., the P.D. of electrodes being 557 and 668 volts, and q (distance of foot of positive column from cathode) 7 and 8 respectively.

The electric forces in the two positive columns were found (section 12) by placing the electrodes 11·6 cm. apart and determining the reduction in the battery required to give the same extraordinary current 1·186 m.a., and again the reduction required to give the same ordinary current ·883. These reductions were found to be 87 and 190 volts respectively, giving as the respective forces 8·5 and 18·6 volts per cm. To check these results the electrodes were placed 16·8 cm. apart, whereupon the batteries required to reproduce the same currents proved to be 939 and 900. These results show that the ordinary force is fairly accurately determined (within 3 or 4 per cent.), but that the extraordinary force is subject to much larger variations, being probably within 10 per cent. of the value 7·7 volts per cm. (See section 5 above.)

At the end of these experiments the pressure had fallen to ·74, so that there may have been 5 per cent. of ozone in the gas during the last mentioned determinations.

It should be added that when the electrodes were only 7·7 cm. apart no alternative currents were obtained. This confirms what has been already established, that alternative currents in the same circuit in oxygen is a phenomenon of the positive column, practically at least.

(iv.) $p=1{\cdot}04$ mm., $D=19{\cdot}7$, distance of S from cathode $=7$ cm. Alternative currents observed were ·552, ·248; ·524, ·271; ·530, ·226: corresponding E.P.D.'s, 488, 770; 515, 750; 510, 791.

23. After these and a few other experiments, the apparatus was accidentally broken at the anode end. It was very ably repaired by Messrs. Townsend & Mercer's glass-blowers, and was reconstructed. A new cathode was inserted, 2·75 cm. in diameter, closely fitting the tube, as stated above. The following are details of some specimen observations.

(v.) $D=21{\cdot}6$, $p=\cdot 61$ mm. The current was made to alternate between 1·075 m.a. ($X=592$ volts) and ·91 ($X=654$); between 1·048 ($X=602$) and ·885 ($X=667$); and eventually only the ordinary ·91 m.a. was obtained.

(vi.) $D=21{\cdot}6$. A little more oxygen was introduced bringing p up to ·82, when the current was made to alternate between 1·02 m.a. and ·745, the corresponding E.P.D.'s being 580 and 680 volts. This alternation was frequently produced backwards and forwards. But whereas the ordinary current ·745 was stable and repeatable, the extraordinary varied, assuming the values ·965, ·91, etc., with E.P.D.'s 600, 620, etc.

(vii.) New oxygen. $p=1{\cdot}03$ mm., $D=21{\cdot}5$ cm., $B=1007$ volts. No transition here from the extraordinary current 1·38 m.a. ($X=503$). But the ordinary current ·44 appeared and slowly crept up to the extraordinary ·55, and there remained steady, X changing from 602 to 501 volts. This behaviour suggested that the gas was near the limit of the state which permits alternative currents of this magnitude to pass. These observations have not been included in Table V., since the gradual nature of the change throws doubt on the value of the ordinary current. In all the other cases the change was instantaneous.

The pressure was now reduced to ·84, and D was 20·9. No alternations with the extraordinary current 1·23 m.a. ($X=559$), but alternations easily obtained between ·66 and ·44 (E.P.D.'s 560 and 710); and (with change of resistance in circuit) between ·76 and ·59 (E.P.D.'s 573 and 688); and (another change of resistance) between ·746 and ·564 (E.P.D.'s 583 and 686). Further, with the same specimen of gas and with D and p the same, and the circuit constant, the current was made to pass through the following alternations: ·664, ·442, ·635, ·442, ·63 m.a., and the E.P.D.'s through the values 561, 710, 580, 710, 598 volts. The middle point of S was 6·5 cm. from the cathode.

Subsequently the current went through many alternations between ·608 and ·442 (E.P.D.'s 598 and 710), the distances of the positive columns from the cathode being 5 and 6 cm. in the extraordinary and ordinary currents respectively. And after many discharges the currents become ·59 and ·442 (X's 610 and 710).

These details are given to illustrate more clearly the striking constancy of the ordinary current, as contrasted with the steady diminution of the extraordinary. Thus, while the electrodes have maintained the constant value of 710 volts in the case of the ordinary currents of this long series of alternations, the potential difference of the electrodes during the passage of the extraordinary currents has undergone a steady increase from 560 to 610 volts, a total increase of 9 per cent. in X_e, involving an increase of 30 per cent. in the electric force in the positive column. (See sections 34 ff.) This throws light upon the great discrepancies observable in the determination of the electric forces in the extraordinary positive columns.

During this series of discharges the pressure fell from ·845 to ·82 mm., that is 3 per cent. If this was due to the formation of ozone, there would have been nearly 7 per cent. of ozone present at the end.

We may conclude from these detailed results that while both kinds of currents are perfectly determinate and precise, the ordinary are constant and repeatable, and the extraordinary, on the other hand, depend to a considerable extent on the past electrical history of the gas; for the currents which pass through the gas have an accumulative effect on it, probably due to the production of ozone.

24. The foregoing accounts will sufficiently describe in detail the nature of this peculiar property of oxygen and the method I used to investigate it. Many other similar experiments were made, giving similar results, most of which are collected in Table V.

Notation employed in Table V. and throughout this paper.

Each line in Table V. applies to a fixed circuit as illustrated in fig. 3, permitting alternative steady currents C_0, C_e through the discharge-tube.

p is the pressure in mm. of mercury,

D the distance in cm. between the electrodes,

C_0, C_e are the ordinary and extraordinary currents respectively in milliamperes,

X_0, X_e the voltage-difference of electrodes during the passage of C_0, C_e,

Y_0, Y_e the electric force in volts per cm. in the positive columns of C_0, C_e,

q_0, q_e the distance in cm. from the cathode of the foot (nearest point) of the positive column of C_0, C_e, so that $D-q_0$, $D-q_e$, are the lengths in cm. of those positive columns.

(The above notation is also used without the suffixes, when the nature of the current is not specified.)

B, R are the voltage of the battery, and the total ohmic resistance, of the circuit, respectively.

m.a. denotes as usual milliampere, and

E.P.D. denotes electrodal potential difference (X).

The values of B, R are not given in Table V., because they are incidental features of the phenomenon, and also because they are easily obtained from the equations

$$B = X_0 + C_0R = X_e + C_eR, \quad . \quad . \quad . \quad . \quad (1)$$

whence

$$R = (X_0 - X_e)/(C_e - C_0).$$

For instance, taking the numbers for the pressure ·564 in Table V., we get R=·374 megohm, B=956 volts. The recorded values were ·365 megohm, 948 volts, so that even when C_0 and C_e differ by a comparatively small fraction of their values, B and R are recoverable, if required, within a small percentage.

Remarks about Table V.

25. The range of pressure in this table is that within which the phenomenon of alternative currents was observed. No doubt the range might be extended by a more effective method of producing the transition from extraordinary to ordinary current at pressures greater than 1·04, and from ordinary to extraordinary current at pressures less than ·54 mm.: *e. g.* by using higher or lower voltages than those of anode or cathode to charge the ring S with.

The distance D, separating the electrodes, is, in all but a few cases recorded in Table V., about 20 or more centimetres, but otherwise arbitrary; such distances being great enough for the purpose in view, but not too great for the battery to maintain steady currents in the discharge-tube at the pressures recorded.

TABLE V.

p.	D.	C_0.	X_0.	Y_0.	q_0.	C_e.	X_e.	Y_e.	q_e.
1·04	19·7	·248	770	...	...	·552	488		
1·04	19·7	·27	750	...	...	·524	515		
1·04	19·7	·226	790	...	...	·53	510		
·89	20·8	·86	676	...	6	1·15	569		
·88	21·2	·441	685	...	...	·58	552		
·84	20·9	·44	710	...	...	·66	560		
·84	19·7	·331	687	...	...	·47	558		
·84	20·9	·59	688	...	...	·76	573		
·82	21·6	·745	680	...	6·5	1·02	580		
·81	19·5	·408	625	...	...	·497	540		
·76	21·8	·883	668	18·6	8	1·19	557	8·5	7
·74	19·7	·416	620	...	...	·496	545		
·73	21·2	·855	656	...	...	1·08	576		
·73	21·2	·662	660	...	...	·81	595		
·72	21·4	·36	674	...	...	·52	524		
·7	21	·359	669	...	7	·496	540	...	6
·65	21·3	·386	651	20·6	...	·53	519		
·61	21·6	·91	654	...	...	1·07	592		
·6	19·7	·82	588	18·3	...	1·06	501	11·8	
·6	23·1	·83	649	18·3	...	1·12	541	11·8	
·6	23·7	·483	681	18·9	...	·705	532		
·59	23·8	·354	680	...	...	·494	550		
·59	20·5	·386	610	...	...	·496	508		
·59	17·1	·398	558	...	...	·450	507		
·58	24·2	·328	685	17·5	...	·46	563		
·58	17·7	·433	568	...	...	·496	510		
·565.....	24·4	·336	687	17·2	...	·485	547		
·564......	22	·91	616	14·6	...	1·1	545	9·3	
·56	18·5	·494	564	17·5	...	·585	502	7·6	
·56	24·8	·48	675	17·6	...	·663	550		
·55	21·5	·99	630	...	...	1·19	555		
·54	21·4	1·1	604	...	8	1·3	533	...	7
·54	21·4	·6	601	...	8	·72	521	...	7

The values of X_0, X_e were in most cases thus determined:—Before passing the current through the discharge-tube T (fig. 3), T was short-circuited by connecting the right and left mercury cups at M, and the current read on the galvanometer. Let this reading be K. If now on insulating these cups the current C_0 passes through the discharge-tube (read on the same galvanometer), X_0 is immediately given by $B(K-C_0)/K$ volts, whatever the constant of the galvanometer. Similarly for X_e.

In the case of the galvanometer thus used, the errors of observation would not have exceeded in general one or two per cent.

The values of Y_0, Y_e in Table V. were determined by the method explained in section 12. But in reproducing, *e. g.* the current C_0 in the discharge-tube, when B and D are suitably reduced, C_e will be altered; for the ratio of C_0 to C_e diminishes with the length of the positive column. In applying this method, if no transition of current is producible with reduced B and D, it is at least necessary to know whether the current that appears is the ordinary one or the extraordinary.

As for q_0, q_e, the discharge is often so faintly luminous that it is difficult to be sure of their values within ·5 cm. Still, the positive columns of both ordinary and extraordinary discharges look perfectly regular and determinate. And when the transition is effected backwards and forwards, the extraordinary positive column shrinks back about 1 cm. and distinctly gains in brightness, and then moves forward again as it resumes its paler shade. (See section 30 below.)

26. The currents C_0, C_e change freely when the ohmic resistance R is varied. The ratio C_e/C_0. always greater than unity, is not a simple one. It diminishes as the positive columns are shortened, that is as the anode is brought nearer the cathode, and tends towards unity when the positive columns are thus made to disappear. Moreover, as shown above (section 23, vii.), C_0 remains constant after many discharges have passed through the gas, whereas C_e undergoes a steady increase, so that the ratio tends to increase, when the circuit remains unchanged, through the electrification of the oxygen. With D about 20 cm., the pressure ranging from ·5 to 1 mm., and currents not exceeding a milliampere, the ratio of C_e to C_0 should range from about 1·2 to 1·5.

27. The E.P.D., X_0, during the ordinary discharges, is nearly independent of the current C_0, when the latter's range of variations is that of Table V. At least, X_0 only varies by a small percentage. This is shown by Table V. It is also accordant with the results obtained and discussed

in section 14 above, which show that Y_0 is only to a limited extent dependent on currents of our order of magnitude. For X_0 is roughly equal to Y_0, multiplied by the length of the positive column, plus the constant cathode fall of potential; so that percentage variations in Y_0 produce in our discharges less than half such variations in X_0, since the fall of potential down the positive column, $(D-q_0)Y_0$, was in every case less than the cathode fall, and Y_0 can only be affected to the extent of 3 per cent. by the variation of current shown in Table V. Hence any considerable percentage discrepancies in the values of X_0 in Table V. must be attributed to other causes.

The same might be true of X_e and C_e, if it were not for their tendency to undergo accumulative changes under the action of the discharge.

Some General Details.

28. During the experiments represented in Table V., it was verified that when once the discharge had started or had been transformed from the ordinary to the extraordinary or *vice versa*, it was not affected either by insulating the ring S from anode or cathode, or by earthing it. Hence the ring, though useful for starting the discharge or transforming it, does not disturb the discharge appreciably.

A curious effect may be noticed. When the distance between the electrodes was too great for the discharge to start with the battery B (about 1000 volts), at a certain pressure (*e.g.* 1·04 mm.), the discharge was easily started by connecting S to the anode. But after being stopped it would not restart in the same way till this connexion had been broken and the ring S earthed or connected to the cathode. This effect was doubtless due to electrons adhering to the inner surface of the discharge-tube in the neighbourhood of S, so long as it was at a positive potential, and so neutralizing to some extent the electric force set up in the gas between the cathode and the ring.

Position of the Ring S.

29. It was observed that the ring had to be near the foot of the positive column to effect the alternation of current. If S is one or two cm. up the column, only the ordinary current would appear on connecting S to the anode. On the other hand, if S was one or two cm. nearer the cathode,

the extraordinary started on connecting S to the cathode but then stopped.

Generally speaking, S was best placed just outside the positive column of the (longer) extraordinary discharge, so that the foot of the column of the ordinary discharge fell about a cm. short of it.

Positive Columns of Alternative Currents contrasted.

30. When the transition from the ordinary discharge to the extraordinary takes place, the current increases in magnitude, and the positive column increases about a cm. in length and loses in brightness. This latter effect is paradoxical, for the general effect of increasing the current through a gas is to increase the brightness of the positive column. The explanation must be that the intensity of the brightness of the positive column depends not only on the current-strength but also on the electric force within the positive column, and that the great reduction of this force, when the transition in question takes place, more than balances the increase of current.

In the case of ordinary positive columns, I have occasionally observed striæ of a type peculiar to oxygen. They are thin luminous disks and not curved. They are a very pretty phenomenon. In my first paper (Phil. Mag. April 1908, p. 565) I mentioned some so close together that 10 were within 1·8 cm. These appeared at ·8 mm. about, with the zinc electrodes. On the present occasion, at the pressure ·27 mm., I noticed similar band-like striæ about 2 mm. thick and about 8 mm. apart in considerably used oxygen, the current being ·247 m.a.; and also at the pressure ·55, current ·276 m.a., striæ much closer together, namely 3½ to the cm. I have not observed striæ in the columns of extraordinary discharges.

Transition of Current Effected by touching the Discharge-tube.

31. In earlier experiments the alternative current was produced by simply touching the discharge-tube during the passage of the extraordinary current. About half of these observations are given in Table VI., the rest of them being omitted because they agree so closely as to be practically repetitions. In every case the distance between the electrodes was 20 cm., the battery was 990 volts and the total ohmic resistance, including that of the galvanometer (36,240 ohms), was ·911 megohm.

TABLE VI.

D=20 cm, B=991 volts, R=·911 megohm.

p.	$C_e \longrightarrow$	C_0	$X_e \longrightarrow$	X_0
1·4	·463	...	568	
1·25	·535	...	501	
1·08	·543	...	531	
·91	·524	·309	510	706
·88	·5	·334	531	683
·83	·522	·373	511	647
·82	·524	·364	510	656
·8	·505	·389	527	633
·76	·508	·389	524	633
·75	·539	·386	500	639
·73	·5	·4	532	623
·72	·539	·401	499	624
·7	·502	·392	531	632
·65	·529	·408	507	618
·64	·521	·416	515	611 *
·6	·522	·417	514	611
·59	...	·418	...	610
·58	...	·420	...	608

Transition of current effected by touching the discharge-tube.

*** This transition of extraordinary to ordinary current was spontaneous.**

Other transitions of greater currents were effected by keeping a finger on the discharge-tube, but the transition was reversed on removing the finger. Thus at the pressure ·8 mm. the current (C_e) 1·37 m.a. changed into ·99 (C_0), the E.P.D. (X_e) 492 changing into (X_0) 628; and similar effects were obtained between ·7 and ·91 mm. These observations illustrate the rule stated in section 14, that the greater the current, the lower the pressure at which it appears spontaneously as an ordinary discharge.

Again, between ·7 and ·81 mm., both currents showed a tendency to diminish slowly. In this region of pressure the discharge readily undergoes transition. In such cases the mean value of the observed currents is given in Table VI., which, however, only differ from the extreme values by about 2·5 per cent.

General Results.

32. The uppermost curve of fig. 6 is the mean curve determined by all the values of X_0 corresponding to pressures between ·25 and 1·04 mm. for the electrodal distance 20 cm., the current being adjacent to ·5 m.a. but otherwise arbitrary; for with this condition we have seen that the E.P.D. is practically independent of the current. These values are obtained from Tables III., V. and VI. Table III. determines the portion AB of the curve accurately as fully explained in section 21. Table VI., which applies to D=20 cm., determines the points on fig. 6 which are indicated by dots; and of these, those which belong to ordinary discharges lie close to the upper part of AB or to B*a* which is a continuation of AB.

In the case of Table V., it is necessary to decrease (or increase) the value of X_0, corresponding to any electrodal distance D by $(D-20)Y_0$, in order to make it apply to D=20 at the same pressure; where Y_0 is the electric force in the positive column of the current in question. For this purpose of adjustment, Y_0 may be taken from Table V., or from the curve of fig. 4, or from the formula $Y_0=(X-413)/(D-q_0)$, when p exceeds ·65 mm. (See section 37 below.)

The values of X_0 thus contributed by Table V. (about thirty), when plotted against their pressures, determine points which all lie close to the curve, or within 3 per cent. of those values from the curve, except about two which differ by five per cent. from the ordinates of the curve. Hence we may say that the curve is the locus of the points p, X_0 given by all our observations within the errors of those observations.

These results prove that the ordinary currents are determinate features of oxygen, and are not dependent on the means used to produce them. Nor are they affected, at least to any great extent, by the past electrification of the gas.

33. On the other hand, when the extraordinary currents are passing, the E.P.D.'s are by no means so coordinate. This is to be expected from the discordant values of the electric force in the positive columns of such currents, shown in Table I. and fig. 4. The gas seems to be modified by discharges passed through it, so that the current undergoes a gradual decrease and the E.P.D. a gradual increase when a series of discharges are passed through the gas in a fixed circuit. (Section 23, vii.) Now Table III. determines a number of points in fig. 6 whose coordinates are p, X_0, and all of these except one lie close to

the line FE. These points are indicated by the small crosses. In the same way Table VI. gives a number of points shown by the dots, and these approximate closely to FE or its continuation eF, or else lie above the line eFE; and the same thing is true of the large number of points contributed by Table V. after correcting the values of X_e so that they apply to D$=$20 cm. (which correction does not exceed about a volt per mm. increase of D). Hence we may conclude that the line eFE is very nearly the locus of the points whose coordinates are p, X_e, when the electrodes are 20 cm. apart and extraordinary currents of the order ·5 milliampere are passing through oxygen, undisturbed by previous electrification; for the effect of such disturbance is to bring those points above that line.

It follows that the ordinary and extraordinary currents in a given circuit are two stable forms of discharge which oxygen in a conducting state may assume, the one form being practically unaffected by, and the other modified in an accumulative manner by, previous discharges through the gas.

Deduction of the Electric Forces in Alternative Currents.

34. From fig. 6 we can deduce approximately the mean normal value of the electric force in the positive columns of the alternative discharges in fixed circuits, studied in this paper (additional to the values of Table I.).

For the value of Y_0 can be derived approximately from the value of X_0, if q_0 is known, by means of the equation

$$Y_0 = (X_0 - F)/(D - q_0), \quad . \quad . \quad . \quad . \quad (2)$$

where F is the value of the E.P.D. when $D = q_0$ and the current is the same, so that the positive column has just disappeared. And if the current is only roughly the same, that is of the same order, equation (2) will be still nearly correct *, X_0 being only to a limited extent dependent on the current. (Section 27.)

Now F is nearly constant in oxygen with our range of pressure and current. This is shown in Table IV., and by the curve UuV in fig. 5, which represents that table graphically, applying to discharges between electrodes 7·9 cm. apart. For q_0 is about 8 cm. for pressures below ·65 mm., and decreases to 6 cm. as the pressure rises from ·65 to 1 mm.

---

* Where there are striæ in the positive column, equation (2) would give the average value of Y_0, or, *mutatis mutandis*, of Y_e. But in oxygen striæ seldom appear (see section 30), at least at our pressures, so that the force within the positive column of both ordinary and extraordinary currents may be assumed to be constant.

35. The lowest E.P.D. in the curve alluded to in fig. 6 is 413 volts[*], namely when $p = {·6}$ to ·65 mm. When p is less than this, the E.P.D. slightly increases, probably because the cathode fall of potential is becoming more than the "normal cathode fall," the current being more than sufficient to cover the cathode. And as p increasingly exceeds ·6 mm., a portion of positive column makes its appearance, increasing up to 3 cm.; for these discharges, being self-determined, would have been at such pressures extraordinary currents (see Table III.), and q_0 is about 5 cm. when $p = 1$ mm. (Table V.).

36. From these considerations it follows that for pressures below ·65 mm. (whereabouts the abrupt change tends to take place, from ordinary to extraordinary current) the electric force in the ordinary positive column is equal to the difference of the ordinates of the upper and lower curves, AB, Uu, of fig. 6 divided by the difference between the electrodal distances (20, 7·9 cm.) which are constant for these curves, that is by 12·1 cm. In fact, the values of F in equation (2) are practically the same as those of the ordinates of Uu, and q_0 is nearly 7·9 cm. for pressures below ·65 mm.

Again, when the pressure exceeds ·65 mm., the difference of ordinates, at any pressure, of the (straight) curve FE ($D=20$) and the lower curve UV ($D=7·9$) divided by 12·1 gives the electric force in the extraordinary positive column at that pressure; for both curves now refer to extraordinary currents.

37. The electric force in the positive column of *ordinary* currents when the pressure is above ·65 mm. cannot be deduced correctly by the same method, which would introduce a considerable percentage error (up to 10 per cent. at

---

[*] That the voltage 413 is the value of X_0 when $D=q_0$ and the cathode fall is *normal*, or nearly normal, appears from the following considerations. With platinum electrodes the normal fall in oxygen is 369 (Capstick), and the same figure may be presumed with our gold electrodes. Now the rise of potential between the cathode and the foot of the positive column, in the case of hydrogen and nitrogen, is the cathode fall plus a voltage less than $\frac{1}{2}x$Y, where x is the distance between the negative end of the Faraday dark space and the foot (nearest point) of the positive column (See the diagrams in Sir J. J. Thomson's 'Conduction of Electricity through Gases,' 1903, c. xv.) In our case with $p=$ ·6 mm., and $Y=18$ volts/cm., x should be less than 6 cm., if we are guided by the behaviour of those other gases. Therefore F should be less than 423. Hence the figure 413 should apply to a discharge with a practically *normal* cathode fall, in order to satisfy the above inequality.

1 mm. pressure) in excess of Y_0. For the ordinate to the curve B*a* (D=20) at a pressure greater than ·65 applies to an ordinary current, and the ordinate at the same pressure to the lower curve (D=7·9) applies to an extraordinary current with a short length of positive column of low electric force. Hence we have to use the formula (2), where F=413, and D=20, although the values of q_0 are only roughly known from Table V. These values are 7, 7, 6 cm. for the pressures ·7, ·8, ·9 mm., involving an error that can scarcely exceed ·5 cm. Thus we derive from equation (2) the values of Y_0, 16·3, 17·2, 20·5 volts/cm., for the pressures ·7, ·8, ·9 ; in which the percentage errors arising from the assumed values of q_0 should be less than 4 per cent. Further, since q_0 must be assumed to lie between 6 and 5·5, when $p=1$ mm., we obtain for Y_0 ($p=1$) the value 23·6.

38. The approximations thus obtained to the values of Y_0, and Y_e, are collected in Table VII.; which also contains, for the sake of reference, the mean values of X_0, and X_e for D=20, and the values of X for D=7·9 cm. The latter are derived from the ordinates of the curve U*u*V, which applies to neutral discharges, neither ordinary nor extraordinary, (for with no positive column no such distinction can be made), except when the pressure exceeds about ·65 mm., when the ordinates are X_e. But this distinction is not made in the table.

Table VII.

(For notation see section 24.)

Currents of order ·5 m.a.

	D=20 cm.		D=7·9.		
p.	X_0.	X_e.	X.	Y_0.	Y_e.
·3	555	...	436	9·8	
·4	565	...	431	11·1	
·5	580	...	420	13·2	
·54	590	509	417	14·3	
·6	608	508	413	16·1	
·65	617	506	415	16·7	7·5
·7	625	504	419	17·0	7·0
·75	633	504	424	17·3	6·6
·8	637	503	427	17·4	6·3
·9	700	502	432	20·5	5·8
1·0	750	501	437	23·6	5·3
1·1	...	500	440	...	5·0

The X_0's, for $D=20$ cm. in Table VII., derived from the upper curve of fig. 6, are the mean results of so many observations that they ought not to be infected with the same percentage errors to which individual observations are liable in electrical experiments on gases at such low pressures; though the errors of observations on *ordinary* discharges are not normally, as we have seen, more than a few per cent.

The values of X_e are approximately the values of the E.P.D. of extraordinary discharges, also of order ·5 m.a., through oxygen unaffected by previous electrification.

The values of Y_0 are in satisfactory agreement with Table I. and fig. 4, except for the discrepancy at the pressure ·6 mm., where the latter gives 18 volts/cm. The value 16·1 of Table VII. agrees accurately with the run of the curve of fig. 4. But in section 15 reasons have been given for not discarding the value 18, and the discrepancy, 1·9 volts/cm., must remain unresolved.

As for the values of Y_e in Table VII., they agree fairly well with the lowest values of Y_e given in Table I. and fig. 4, which are presumably the values of Y_e in oxygen previous to electrification.

39. This general agreement of Table I., all derived from individual experiments described in section 12, with the results of Table VII., deduced from the joint data of so many other observations, shows once more that there are two definite modes of the passage of electricity through oxygen at pressures between a certain range (of which, as so far observed, ·8 mm. is about the centre), and that the gas at such pressures can conduct electricity in the same circuit in one or other of these two modes, which the oxygen may adopt spontaneously or through control, provided that the alternative currents are of certain orders of magnitude.

Influence of a Mixture of Air on the Transition of Current.

40. A few experiments were made to see to what extent oxygen must be pure to permit alternative currents to pass in a given circuit in circumstances where they appear in pure oxygen. Oxygen was mixed with a considerable proportion of air, so that the mixture contained 88·4 per cent. of oxygen and 11·6 per cent. of nitrogen (and argon, etc.). Between the pressures ·81 and ·52 mm., $D=19·8$ cm., currents of extraordinary type and magnitude ·5 or rather less, and of magnitude greater then 1 m.a., passed; but the only transition observed, and that on touching the tube, was at

the pressure ·65, when ·475 m.a. (C_e) changed to ·386 (C_0), the corresponding change of E.P.D. being from 528 (X_e) to 611 volts (X_0). These alternatives are so similar to the numbers given in Table VI. at the same pressure, but with a slightly different circuit (battery and resistance), that we may conclude that the oxygen, even with such a large percentage of nitrogen, had not lost the peculiarity of alternative currents, but had lost the facility of exhibiting it.

No Change of Pressure observed during Transition of Currents.

41. It is natural to suppose that the two different modes of conducting electricity which oxygen possesses at certain pressures may be associated with two different molecular states which the gas might be made to alternate between at those pressures. A change from one such state to the other would be accompanied by a change of pressure, unless it consisted of a passing *pari passu* into ozone and monatomic oxygen, in which case the pressure would remain constant. In order to see whether any change of pressure, detectable by the McLeod gauge, arises with transition of current, the pressure was carefully read during an extraordinary discharge with current of order ·5 m.a. at the pressure ·83 mm., and again about thirty seconds later. The current was then switched without stopping it to the alternative ordinary form, and similar observations were made. The fall in each case was very small, namely of the order ·0016 mm., such as is always to be expected with oxygen in such conditions, and contained in such a volume, which was nearly 600 c.c.

These results prove that no *local* change of pressure occurs during the discharge in the discharge-tube. For such a change would have produced a change of pressure in the oxygen in the bulb of the McLeod gauge (which belonged to the same volume with the discharge-tube), and so could not have escaped detection. But the results do not settle the question whether there may be produced by the discharge, at the moment of transition of the current, a general molecular change, with change of pressure, in the whole mass of the gas filling both discharge-tube and gauge. For in using the latter, the gas in its bulb was compressed to a pressure of 264 mm., at which it would have recovered the ordinary molecular condition of oxygen. Thus whether the latter is assumed to go with ordinary or extraordinary discharges, no change of pressure could be detected by the McLeod gauge. Nevertheless the negative result of these observations of pressure during the discharges of both types makes it most improbable that any molecular change involving change of pressure takes place with transition of current.

42. The phenomena described in this paper are an extension of the effects of which I gave an account in Phil. Mag. April 1908, and summarized in section 2 above. In the latter paper I raised the question whether the electrical discontinuities at about ·8 mm. were connected with the discontinuity in conforming to Boyle's law in oxygen at the pressure ·7 mm., described by C. Bohr in *Wied. Ann.* vol. xxvii. p. 459 ff. (1886), and confirmed by other physicists, although Lord Rayleigh with the most careful investigation and with Bohr's result in his mind entirely failed to discover any such departure from Boyle's law in the neighbourhood of ·7 (Phil. Trans. 1901, p. 205). The results established in the present paper, however, show that the abrupt changes of current are not discontinuities in the strict sense of the word, but sudden shifts from one to the other of two possible modes of conduction of electricity through the oxygen at certain pressures and with certain orders of current associated with those pressures. Both these modes are regular and continuous with continuity of pressure; but the one is constant and the other is liable to modification by the past treatment of the gas. If these *are* associated with different molecular states, one of those molecular states, that of the ordinary currents, might conform to Boyle's law consistently, but not necessarily the other.

In conclusion, I wish to express my obligations to Mr. E. P. Cardew, who helped me in the early part of this research and established the very suggestive fact that the transition from extraordinary current to ordinary could be effected by touching the discharge-tube.

All the experiments were made in the writer's private laboratory in Saham Toney Rectory, Norfolk. The battery used in this and other researches was practically covered by a grant from the Royal Society in 1911, made originally for an investigation connected with the positive column of oxygen, and I wish to express my thanks for it in this paper.

LXXXIII. *An Application of Diffraction Halos to Elasticity.*

By Jas. P. Andrews, *B.Sc*, *East London College* *.

WHEN lycopodium is dusted on any polished plane surface, the image of a small light placed in front of it appears surrounded by circular coloured rings. On deforming the surface in any way, the rings change their shape, and some measure of the strain may thus be obtained. The following describes how Poisson's Ratio may be determined by this method.

The halos here obtained are formed in the same manner as those seen in a mirror with a silvered back, whose front surface is dusted with fine powder, and which have been fully described and explained by Stokes †. The illuminated particle sends secondary wavelets to the eye both directly and by way of the regularly reflecting surface, the retardation between these two routes determining the colour seen. It is at once clear that light of wave-length λ, and of a given order of interference, will issue from the surface at a particular angle, α_λ, with the normal at that point. Then if the surface bends and the normal be made to rotate, the angle at which the rays enter the eye must change and the halo be deformed.

A uniform rectangular brass plate P, one surface of which is polished and dusted with lycopodium, is bent by couples at its ends, and placed a few feet from a small light L_1. An observer at E (fig. 1) can measure the diameters of the elliptical halos upon the superposed image of the screen S, which is seen by reflexion in the glass plate G. S is an opaque screen, pierced by two perpendicular rows of fine equidistant holes, illuminated by light L_2. The distance of S from G may be arranged so that parallax between the images of S and L_1 is quite small.

The observer measures the lengths of the major and minor axes of one of the coloured bands, and then bends the plate a little more and repeats the measurement. Let x be the angle subtended at the eye by the diameter which is in the plane of bending, and y that subtended by the perpendicular diameter. On bending further, let these change to x' and y'. Then

$$\text{Poisson's Ratio } \sigma = \frac{\dfrac{1}{y'} - \dfrac{1}{y}}{\dfrac{1}{x} - \dfrac{1}{x'}}.$$

---

* Communicated by the Author.

† G. G. Stokes, Math. and Phys. Papers, vol. iii. p. 174.

For if OPQ is a portion of the surface (fig. 2), and x is the angle subtended by the diameter considered, let C be the

Fig. 1.

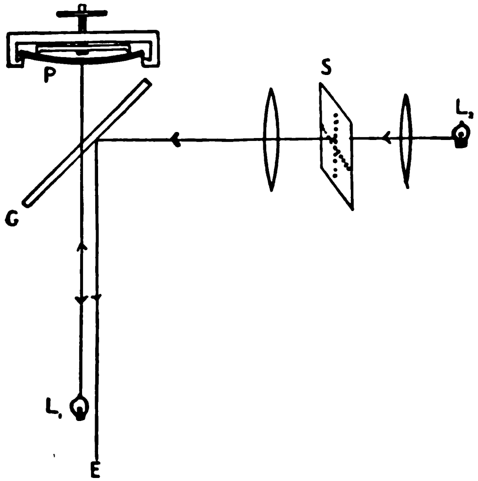
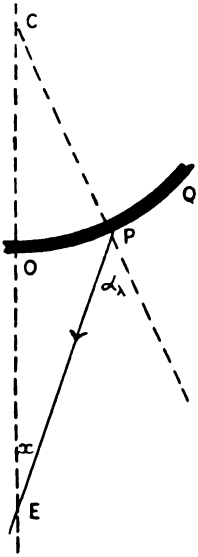


Fig. 2.



centre of curvature of the surface, whose radius of curvature is r, and let $OE=d$, the distance of the plate from the eye.

Angle EPQ $= \alpha_\lambda$, and $\alpha_\lambda = x + \frac{\mathrm{OP}}{r} = x + \frac{xd}{r}$ approximately;

hence $\frac{\alpha_\lambda}{x} = 1 + \frac{d}{r}$: similarly $\frac{\alpha_\lambda}{x'} = 1 + \frac{d}{r'}$.

Therefore

$$\alpha_\lambda\left(\frac{1}{x} - \frac{1}{x'}\right) = d\left(\frac{1}{r} - \frac{1}{r'}\right).$$

Similarly for a direction at right angles,

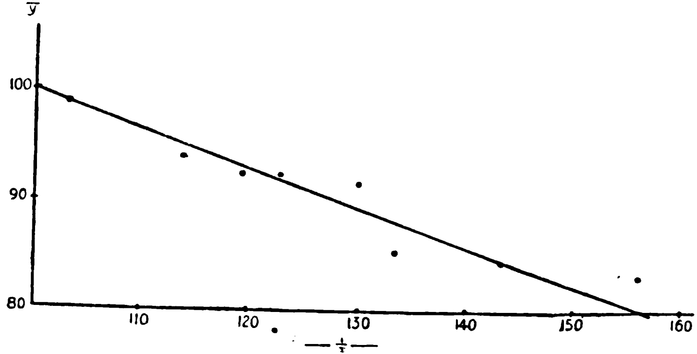
$$\alpha_\lambda\left(\frac{1}{y} - \frac{1}{y'}\right) = d\left(\frac{1}{\mathrm{R}'} - \frac{1}{\mathrm{R}}\right).$$

Now $r = \sigma\mathrm{R}$ and $r' = \sigma\mathrm{R}'$; so that finally

$$\frac{\frac{1}{y'} - \frac{1}{y}}{\frac{1}{x} - \frac{1}{x'}} = \sigma.$$

The halos are generally small and diffuse, and do not improve on bending the plate; great accuracy cannot therefore be attained. The graph below shows a series of results, $\frac{1}{y}$ being plotted against $\frac{1}{x}$.

Fig. 3.



The results of six series of this kind are as follows:—

$$\sigma = \cdot 40, \cdot 48, \cdot 37, \cdot 33, \cdot 37, \cdot 25;$$

mean value of $\sigma = \cdot 37$.

Although the method is capable of some improvement, it is presented rather as an interesting variant of the usual experiments with the diffraction halo.

LXXXIV. *The Striated Distribution of Space Charge.*
By B. M. CASSEN [*].

SUMMARY.

IT is shown that, in the statistically steady state, striations will, in general, exist in an electric discharge, even when the rate of ionization is constant at all points along it. The case where one ion is much more mobile than that of the opposite sign is treated analytically. An exact solution of the equations expressing the electric potential as a function of the distance along the discharge is obtained in terms of elliptic functions. The formula, involving the complete elliptic integral for the real period of the potential, gives an exact expression for the distance between the striations as a function of physical quantities determining the state of the discharge. The condition that the rate of ionization in the discharge is constant along it does not prevent the application of the analysis to ordinary discharges, if account is taken of ionization by radiation as well as by collision. A practical form of the formula for the distance between the striations shows why that distance varies roughly as the inverse square root of the pressure, why the striations usually tend to become concave towards the anode, why the striations become closer together in a constriction in the tube, and why they are affected by small amounts of foreign gases; it also predicts a separation of the striations with increasing temperature.

IN general, for a discharge in the steady state, electrically and thermally, between two plane-parallel electrodes through a gas which is ionized into one type of positive ion and one type of negative ion in equilibrium, with respect to their rates of formation and recombination, the following relations hold:

$$\frac{d^2V}{dx^2} = 4\pi(\rho_2-\rho_1), \quad \ldots \ldots \quad (1)$$

$$I_1 = \rho_1 v_1, \quad \ldots \ldots \quad (2)$$

$$I_2 = \rho_2 v_2, \quad \ldots \ldots \quad (3)$$

$$I = I_1 + I_2, \quad \ldots \ldots \quad (4)$$

$$\rho_1\rho_2 = \epsilon_1\epsilon_2\frac{q}{\alpha} + \frac{\epsilon_2}{\alpha}\frac{dI_1}{dx} = K, \quad \ldots \quad (5)$$

---

[*] Communicated by Prof. S. Chapman, M.A., D.Sc., F.R.S.

where V is the potential in electrostatic units at a point x cm. from the cathode, relative to the cathode,
ρ_1 is the density of positive electricity in electrostatic units per cm.^{3},
ϵ_1 is the charge of the positive ion in electrostatic units,
v_1 is the mean velocity of positive ions,
I_1 is the current per cm.^{2} carried by positive ions,
ρ_2, ϵ_2, v_2, I_2 have similar significance, but pertain to the negative ion,
q is the number of ions produced in one cm.^{3} in one second,
α is the recombination coefficient of the ions.

Equation (5) is simply the particular case, for the steady state, of the well-known equations forming the basis of the simple theory of ionized gases as given by J. J. Thomson *, and no remarks are necessary on the first four equations.

Considering V, ρ_1, ρ_2, I_1, I_2, v_1, and v_2 as functions of x, but I and K independent of x, in the steady state, there are five independent relations connecting these seven functions of x. It is necessary to have two more relations to determine these quantities completely as functions of x. Of course, the truth of (5) precludes those cases where the mean free paths of the ions are comparable with the distance between the electrodes, so that there is no simple relation connecting V with v_1 and v_2 as there is at extremely low pressures.

Attempts † have been made to develop the theory of the distribution of potential along a discharge by assuming that the ions have constant mobilities μ_1 and μ_2 respectively, giving as the two relations to complete the theory

$$\left.\begin{aligned} -v_1 &= \epsilon_1\mu_1\frac{dV}{dx} \\ v_2 &= \epsilon_2\mu_2\frac{dV}{dx} \end{aligned}\right\} \quad \ldots\ldots \quad (6)$$

This procedure does not give very satisfactory results, which could, in fact, hardly be expected, in view of the fact that μ_1 and μ_2 are unknown functions of ρ_1, ρ_2, v_1, and v_2, and cannot be taken as constants with respect to these, especially to the first two. J. J. Thomson ‡ has more recently used

---

* See 'Conduction of Electricity through Gases.'

† See J. J. Thomson, *loc. cit.*

‡ Phil. Mag. xlii. p. 986 (1921).

relations based on the probability of an ion retaining a certain portion of its kinetic energy in the direction of the field, after impact. He does not assume that q is constant, and the way in which he assumes it to vary with the potential gradient and current density introduces a periodicity into the nature of the discharge. The assumption only takes into account part of the ionization. The principal other source of ionization is the radiation emitted by recombination of ions. This and other effects that have been studied in low voltage arcs evidently tend to smooth out the production of new ions, so that in most cases it would seem that the actual conditions in the positive column of a discharge or in a low voltage arc can be fairly approximated by assuming q independent of x. As will be seen in what follows, it is possible for striations to exist in a discharge even when this assumption is made, and in general they must always be present except in a particular case where the period of the striations becomes infinite.

When the positive ions, for example, have a negligible mobility in comparison with the negative ions, then r_1 can be assumed to be practically zero, and it is only necessary to obtain one valid relation to solve the equations. This case will be the only one fully treated in this paper. A final relation can be obtained from purely statistical considerations applied to the distribution of the positive ions in the field. Boltzmann's distribution law gives immediately for the region of the discharge under consideration

$$\rho_1 = \gamma e^{-\frac{\epsilon_1 V}{kT}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where k is Boltzmann's constant, T the absolute temperature, and γ a constant. To evaluate γ, let V_M and V_m be the maximum and minimum potentials in the region under consideration, then in this region the average value of the charge density of positive electricity is

$$R_1 = \frac{1}{V_M - V_m}\int_{V_m}^{V_M} \rho_1 \, dV = \frac{\gamma k T}{\epsilon_1 (V_M - V_m)}\left[e^{-\frac{\epsilon_1 V_m}{kT}} - e^{-\frac{\epsilon_1 V_M}{kT}}\right].$$

Therefore $\quad . \quad . \quad . \quad (8)$

$$\gamma = \frac{\epsilon_1 R_1}{kT} \cdot \frac{V_M - V_m}{e^{-\frac{\epsilon_1 V_m}{kT}} - e^{\frac{\epsilon_1 V_M}{kT}}} = \frac{\epsilon_1 R_1}{kT} \cdot W, \quad . \quad . \quad (9)$$

where

$$W = \frac{V_M - V_m}{e^{-\frac{\epsilon_1 V_m}{kT}} - e^{\frac{\epsilon_1 V_M}{kT}}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Substitution of (5) in (1) gives

$$\frac{d^2V}{dx^2}=4\pi\left(\frac{K}{\rho_1}-\rho_1\right), \quad . \quad . \quad . \quad . \quad (11)$$

and on eliminating ρ_1 by means of (7), we get

$$\frac{1}{4\pi}\frac{d^2V}{dx^2}=\frac{K}{\gamma}e^{\frac{\epsilon_1 V}{kT}}-\gamma e^{-\frac{\epsilon_1 V}{kT}}, \quad . \quad . \quad . \quad (12)$$

the first integral of which is readily obtained as

$$\frac{\gamma\epsilon_1}{8\pi K\,kT}\left(\frac{dV}{dx}\right)^2=e^{\frac{\epsilon_1 V}{kT}}+\frac{\gamma^2}{K}e^{-\frac{\epsilon_1 V}{kT}}-C_1, \quad . \quad . \quad (13)$$

where C_1 is an integration constant. If the cathode surface, at which V is taken as zero, freely emits electrons, it is necessary, for a steady saturation current of electrons, that $\frac{dV}{dx}=0$ at that surface, in a manner exactly similar to the way in which the thermionic current from a hot cathode is controlled. Thus V and $\frac{dV}{dx}$ vanish simultaneously; using this fact to evaluate C_1 in (13), we get

$$C_1=1+\frac{\gamma^2}{K}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

In a low voltage arc a hot cathode is present and no difficulty is encountered. In an ordinary discharge a surface at which $\frac{dV}{dx}$ vanishes must be taken as the place from which V is measured. The complete solution of (13), after inserting the value of C_1 as given by (14), is

$$\sqrt{\frac{8\pi K\,kT}{\gamma\epsilon_1}}(x+C_2)=\int\frac{dV}{\sqrt{e^{\frac{\epsilon_1 V}{kT}}+\frac{\gamma^2}{K}e^{-\frac{V}{kT}}-\left(1+\frac{\gamma^2}{K}\right)}}, \quad . \quad . \quad . \quad (15)$$

where C_2 is an integration constant.

If

$$y=e^{\frac{\epsilon_1 V}{kT}} \quad \text{and} \quad H=\frac{\gamma^2}{K},$$

the integral becomes

$$\frac{kT}{\epsilon_1}\int\frac{dy}{\sqrt{y(y+1)(y+H)}},$$

which is a simple elliptic integral expressible in the Jacobian form

$$\frac{2kT}{\epsilon_1}\,\mathrm{sn}^{-1}\left(\sqrt{\frac{y}{y+H}},\ \sqrt{1-H}\right)\quad\text{when } H<1,$$

or $$\frac{2kT}{\epsilon_1\sqrt{H}}\,\mathrm{sn}^{-1}\left(\sqrt{\frac{y}{y+1}},\ \sqrt{\frac{H-1}{H}}\right)\quad\text{when } H>1.$$

In the two cases respectively, expressing y as a function of x and replacing y by $e^{\frac{\epsilon_1 V}{kT}}$,

$$\left.\begin{aligned} e^{\frac{\epsilon_1 V}{kT}} &= H\,\mathrm{sc}^2\left[\sqrt{\frac{2\pi K\epsilon_1}{\gamma kT}}(x+C_2),\ \sqrt{1-H}\right],\\ e^{\frac{\epsilon_1 V}{kT}} &= \mathrm{sc}^2\left[\sqrt{\frac{2\pi K\epsilon_1 H}{\gamma kT}}(x+C_2),\ \sqrt{\frac{H-1}{H}}\right],\end{aligned}\right\}\qquad(16)$$

where sc is the usual notation for $\frac{\mathrm{sn}}{\mathrm{cn}}$. If $V=0$ when $x=0$, then the corresponding values of C_2 are given by the multiple valued functions

$$\left.\begin{aligned} C_2 &= \sqrt{\frac{\gamma kT}{2\pi K\epsilon_1}}\,\mathrm{sc}^{-1}\left(\frac{1}{\sqrt{H}},\ \sqrt{1-H}\right),\\ C_2 &= \sqrt{\frac{\gamma kT}{2\pi K\epsilon_1 H}}\,\mathrm{sc}^{-1}\left(1,\ \sqrt{\frac{H-1}{H}}\right),\end{aligned}\right\}\ .\qquad(17)$$

It is evident that the proper value of C_2 cannot be purely real for, if it were, the potential would become infinite periodically at the zeros of $\mathrm{sn}\,x$ and $\mathrm{cn}\,x$; (16) shows that unless $H=1$, the potential will be a periodic function of the distance with a real finite period depending upon quantities determining the physical state of the discharge. If the potential is periodic, evidently its derivatives are periodic with the same period. Therefore, the density of positive ions and the places where there occurs a preponderence of recombination of ions will be periodically distributed, thus giving a quantitative explanation of the very regularly striated positive columns and low voltage arcs commonly observed in electrical discharges. As the real period of $\mathrm{sc}(x, r)$ is $4\mathrm{sn}^{-1}(1, r)$, the distance P between the striations follows from (16), after putting $H = \frac{\gamma^2}{K}$, in the form

$$\left.\begin{aligned} P &= \sqrt{\frac{8k}{\pi\epsilon_1}} \cdot \sqrt{\frac{T\gamma}{K}} \cdot \mathrm{sn}^{-1}\left(1, \sqrt{1-\frac{\gamma^2}{K}}\right), \\ P &= \sqrt{\frac{8k}{\pi\epsilon_1}} \cdot \sqrt{\frac{T}{\gamma}} \cdot \mathrm{sn}^{-1}\left(1, \sqrt{1-\frac{K}{\gamma^2}}\right). \end{aligned}\right\} \quad (18)$$

These formulæ are exact. They can be simplified by certain approximations. By taking $V_m = 0$ and noting that V_M is, in most applications, of the order of 10^{-2}, it is seen from (9) that γ is nearly equal to $\frac{\epsilon_1 R_1 V_M}{kT}$, and taking $\epsilon_1 = \epsilon_2 = \epsilon$ (the elementary charge), which is usually the case, (18) becomes

$$\left.\begin{aligned} P &= \frac{1}{\epsilon} \cdot \sqrt{\frac{8}{\pi}} \cdot \sqrt{R_1 V_M} \cdot \sqrt{\frac{d}{q}} \cdot \mathrm{sn}^{-1}\left(1, \sqrt{1-\frac{\alpha}{q}\left(\frac{R_1 V_M}{kT}\right)^2}\right), \\ P &= \frac{k}{\epsilon} \cdot \sqrt{\frac{8}{\pi}} \cdot \frac{T}{\sqrt{R_2 V_M}} \cdot \mathrm{sn}^{-1}\left(1, \sqrt{1-\frac{q}{\alpha}\left(\frac{kT}{R_1 V_M}\right)^2}\right). \end{aligned}\right\} \quad . \quad . \quad . \quad (19)$$

If S_2 is the density of negative electricity at the point where ρ_1 takes its average value R_1, then

$$\frac{q}{\alpha} = \frac{R_1 S_2}{\epsilon^2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and if ρ_1 and ρ_2 take their average values near the same point, then

$$\frac{q}{\alpha} = \frac{R_1 R_2}{\epsilon^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where R_2 is the average density of negative charge. Putting (20) in (19) gives

$$\left.\begin{aligned} P &= \sqrt{\frac{8}{\pi}} \cdot \sqrt{\frac{V_M}{S_2}} \cdot \mathrm{sn}^{-1}\left(1, \sqrt{1-\frac{R_1}{S_2}\left(\frac{\epsilon V_M}{kT}\right)^2}\right), \\ P &= \sqrt{\frac{8}{\pi}} \cdot \frac{k}{\epsilon} \cdot \frac{T}{\sqrt{R_1 V_M}} \cdot \mathrm{sn}^{-1}\left(1, \sqrt{1-\frac{S_2}{R_1}\left(\frac{kT}{\epsilon V_M}\right)^2}\right). \end{aligned}\right\} \quad (22)$$

As $\left(\frac{kT}{\epsilon V_M}\right)^2$ is usually of the order 10^{-4}, it is seen that the type of striation given by the second of the formulæ of

(22) is the one of practical importance. Fixing attention on this formula, as $\frac{S_2}{R_1}\left(\frac{kT}{\epsilon V_M}\right)^2$ will usually be small (unless there is an extremely large electron density compared with the density of positive ions), then the modulus

$$\sqrt{1-\frac{S^2}{R_1}\left(\frac{kT}{\epsilon V_M}\right)^2}$$

is almost equal to unity, thus making the complete integral large. Since, when r is near unity, $\mathrm{sn}^{-1}(1, r)$ is approximately* equal to $\log\frac{4}{\sqrt{1-r^2}}$, the formula for P becomes

$$P=\sqrt{\frac{8}{\pi}}\cdot\frac{k}{\epsilon}\cdot\frac{T}{\sqrt{R_1 V_M}}\cdot\log\left(\frac{4\epsilon V_M}{kT}\sqrt{\frac{R_1}{S_2}}\right), \qquad (23)$$

or inserting some numerical values

$$P=2\cdot58\times10^{-7}\cdot\frac{T}{\sqrt{R_1 V_M}}\cdot\log\left(\frac{1\cdot4\times10^7 V_M}{T}\cdot\sqrt{\frac{R_1}{S_2}}\right). \qquad (24)$$

This formula shows that the distance between the striations should increase almost linearly with the absolute temperature and vary almost inversely as the square root of the partial pressure of the positive ions. If the latter is proportional to the total gas pressure, then P will vary inversely as the square root of the pressure. This variation† is actually frequently observed. The variation with the temperature could be easily tested experimentally. Equation (24) is consistent with Goldstein's law ‡. It is well known that striations are affected near the glass walls of a discharge-tube. This theory would indicate that, besides a temperature effect, if the glass had a catalytic effect on the rate of recombination of the ions, then α would be increased near the walls. As reference to the second formula of (19) will show, an increase in α tends to make the modulus of the complete elliptic integral become nearer to unity, thereby increasing P. This will obviously tend to make the striations concave towards the anode. This is exactly what is observed. In the same way, if a foreign gas either increases the rate of recombination or decreases the rate of formation or both, the distance between the striations will be greater in presence of the impurity. If the impurity has an ionization potential differing markedly from the gas giving the striations the effect can become very important.

---

* See Cayley's 'Elliptic Functions,' p. 47 (1896) for an elementary demonstration.

† *E.g.* Willows, Proc. Camb. Phil. Soc. p. 302 (1900).

‡ See J. J. Thomson's 'Conduction of Electricity Through Gases,' p. 465.

The period is independent of the current density as such, but can easily be affected by it by the change caused in q and T. If the temperature is kept constant an increase in q in (19) will tend to decrease the period. This evidently explains the effect of the striations frequently becoming closer together in parts of a discharge tube that are narrower than the rest of the tube. The effect of an increase in the rate of ionization, causing the striations to move closer together, indicates a method of experimentally studying the absorption of ionizing radiation in ionized gas.

If the positive ions move appreciably under the electric field, the general theory becomes extremely complicated. But, if the positive ion current does not vary much with the distance, it is possibly permissible to apply the above theory in a moving coordinate system moving with the positive ions. The qualitative result would presumably be moving striations having the velocity of the positive ions, but many complicating factors would come into play.

LXXXV. *Sound Changes analysed by Records.—II. Voice and Violin.* *By* H. M. Browning, *M Sc*, *Ph.D.*[*]

[Plate XVI.]

In the first paper[†], records of sound changes on the cornet and trumpet were considered with special reference to shakes, turns, and iterated notes. In the present paper, some records of changing notes on the violin and by the human voice are shown, together with records of tuning-forks and motions of the diaphragm as obtained by tapping.

The apparatus shows well the change of type of vibration when the pitch of a note is altered; also when one note follows another quickly enough, the period during which the change is taking place is of considerable duration and in all cases is clearly visible. The transition is found to be a slur in all the sung passages, and a jump when one note on a violin is followed by another. This is of interest, as in several cases the sung notes were supposed to be separated by a jump.

---

[*] Communicated by the Author.

[†] "Sound Changes analysed by Records," Phil. Mag. vol. l. Nov. 1925.

The present work has been most useful in emphasizing two things which are necessary in order to obtain good quantitative results of the sounds emitted by the violin. The first is to do away with the human element, and this can be done by mechanical bowing and fingering. The second is to obtain a more sensitive diaphragm, which, although selective, will be sensitive to all the harmonics of a certain fundamental tone, and which will be capable of alteration by change of tension to whatever note is required. In a later research it is proposed to use the apparatus as mentioned above to compare the motions of the string with the sound waves produced in the air by the whole violin.

Theory.—A violin is a much more complicated instrument than a cornet or a trumpet. The latter is essentially an air resonator, whereas the former can be analysed into solid and fluid vibrators, which may act both as forcers and responders.

The strings, when plucked, vibrate with frequencies which are commensurate, and the motion can be represented by the Fourrier Series :—

$$f(x) = y = \sum_{0}^{\infty} a_n \sin\frac{n\pi x}{l} \cos\frac{n\pi x}{l} \sin pt, \quad . \quad . \quad (1)$$

where the value of a_n can be obtained from a knowledge of $f(x)$ for a particular instant of time.

The belly of the violin is asymmetrical, therefore the equation of motion for its free vibration must be of the type

$$\ddot{y} + 2k\dot{y} + p^2y + by^2 = 0. \quad . \quad . \quad . \quad . \quad (2)$$

The solution of this is a harmonic series the frequency of the fundamental differing from $\frac{p}{2\pi}$ by an amount depending upon b and k.

The bridge may be considered as part of the belly, the motion being conveyed by it from the string to the whole resonance chamber. The air inside is still another vibrating system, but it has such a large damping factor that it will follow the vibration of the wood almost as soon as the sound begins.

The equations of motion of vibrations produced at the bridge when the string vibrates may be written as follows :—

$$\left.\begin{array}{l}\dfrac{d^2y_1}{dt^2}+2k\dfrac{dy_1}{dt}+p^2y_1=f_1\sin\left(nt+\phi_1\right)\\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\\ \dfrac{d^2y_m}{dt^2}+2k\dfrac{dy_m}{dt}+\left(mp+h_m\right)^2y_m=f_m\sin\left(mnt+\phi_m\right)\\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\end{array}\right\}\quad(3)$$

This is true for small vibrations, and near the bridge of a violin they certainly are small. Each of these equations will have solutions involving two terms, one, a vibration of frequency equal to that of the forcer, and the other of frequency due to the free vibrations. The latter, being damped, will only be present during the formation of the sound. Thus the motion of the belly and also the air will quickly settle down to a series of commensurate partials of the same frequency as those emitted by the string. However, the amplitudes of these partials will not bear the same relation to one another as those of the string, but will be greater or less as the free period of the belly is near or far away from that of the particular partial.

The motion of the air will be recorded by the diaphragm, but, since the motion of the diaphragm is due to resonance, during the establishment of the vibration the free periods of motion will be present as well as the vibrations forced on it from the air. Because of this the change from one note to another may appear longer than it actually is, as the free vibrations of the diaphragm will persist after the free vibration of the air has died out.

The human voice presents a case similar to that of a trumpet, the larynx in the former having the same function as the lips in the latter. The mouth and nasal resonators act as the tube of the trumpet, and the tongue, palate, etc. form the required space for resonance to different notes.

The tuning-forks were made to vibrate with as large a displacement as possible, thus, because of this and also because of their asymmetry and that of the diaphragm, in many cases the octave and higher harmonics appear.

Experimental Arrangement and Results.—The same experimental arrangement was used as in the cases of the trumpet and the cornet *, but a liliput arc was substituted for the pointolite; thus a more intense beam of light was obtained. The motion of the drum carrying the photographic film was found to have a nearly constant velocity, so that distances measured along the films may be taken as proportional to the time for that portion to pass the slit.

---

* "Sound Changes analysed by Records," Phil. Mag. vol. l. Nov. 1925.

Records were obtained on different days, by tapping the film with a lead shot, and it was found that the fundamental frequency altered with atmospheric conditions. Figs. 1 and 2 (Pl. XVI.) show this. Figs. 3 and 4 are caused by banging the table and by clapping the hands. Fig. 4 shows clearly that a violent motion of the air near the diaphragm does not affect it more than a gentle tap with a lead shot. Thus it may be concluded that the free vibrations of the diaphragm which occur at the start of a note are of comparatively short duration.

If figs. 5 and 2 are compared, it will be noticed that the vibration in 2 is damped out in about five centimetres, whereas in 5, which is the record of a plucked violin string of frequency 192 per sec., the free vibrations have not entirely disappeared until 20 cm. are passed. Thus it may be concluded that at least three quarters of the damping effect is due to the violin, and not to the diaphragm. In cases where the initial amplitude is small, the damping due to the diaphragm will be still less marked.

Several records of the vibration of tuning-forks were taken to try to obtain some information as to the motion of the diaphragm. These records were analysed by Mader's Harmonic Analyser to find what overtones were present. Further, certain plucked and bowed notes on the violin were also analysed. A table below shows the ratio of the harmonics to the fundamental in various cases. Figs. 6 and 7 are records of a tuning-fork of frequency 128 per sec., with and without resonance box. Fig. 8 shows the vibration of 256 fork when far from the diaphragm and then brought near to it; the record clearly indicates the overtones produced in the diaphragm by large vibrations. Fig 9 is a record of the vibration of 512 fork, and the motion appears simple harmonic. The lower trace in fig. 10 and fig. 11 show records of a violin string tuned to C′ 512 vibrations per sec., in the first case plucked and in the second bowed. The type of vibration alters from one record to the other. The plucked note shows decided harmonics, whereas the bowed note appears to contain only simple harmonic vibrations.

Figs. 12 and 13 are records of the bowing and plucking of the G string (192 per sec.). In all of these overtones are present, but the amplitude varies in the different cases. The note G appears in later records of bowing, and again the type of vibration is very much like that of fig. 12. The vibration obtained by plucking the string seems to settle down to a smoother type as shown by fig. 12. Fig. 13 is interesting, as it shows a very pronounced second overtone; this must be due to the pressure applied in bowing the string, and forms a strong advocate for mechanical bowing.

TABLE.

Instrument.	Freq. of Note.	Ratio $\frac{\text{1st Overtone.}}{\text{Fundamental.}}$	$\frac{\text{2nd Ov.}}{\text{Fund.}}$	Remarks.
Fork with box.........	128	·057	nil.	
Fork without box ...	128	·1014	·009	
Small Fork	256	·151	·0158	Far from diaphragm.
,, ,, ...	,,	·323	·093	Near diaphragm.
,, ,, ...	512	·053	nil.	
Violin String (*p*)* ...	512	·22	·12	
,, ,, (*b*) ...	512	·19	·05	
,, ,, (*p*) ...	192	3·3	2·3	
,, ,, (*b*) ...	192	5·5	5·2	
,, ,, (*p*) ...	384	1·05	·31	At beginning.
		·54	·07	Later.
,, ,, (*b*) ...	384	·8	0	

* *p* means plucked, *b* means bowed.

The table seems to show that the fundamental of the lowest note on the violin is weak compared with its first and second overtones, and for some of the other notes the overtones are as powerful as the fundamental. Records of tuning-forks vibrating 320 and 384 per second show very little trace of overtones, so it is to be concluded that they are not produced in the diaphragm because of its asymmetry.

Fig. 14 shows A string (427 per sec.) and G string (192 per sec) plucked successively. The vibration of the upper string had not quite died out when the lower one was started, and it may be this that gives the effect of a wandering overtone (*i. e.* one not quite in tune with the octave of the fundamental) to the vibration of the plucked G string. Fig. 15 shows A (213 per sec.) and G (192 per sec.) bowed successively on the same string, and fig. 16 shows D (288 per sec.) and G (192 per sec.) bowed successively on different strings. The two final notes give traces of approximately the same form, and the fundamental is again seen to be small compared with the overtones. The first notes, D and A, are very different in type, the upper one showing one overtone and the lower one showing many, with the fundamental obscure. On the same string the change from one note to the other was accomplished in $\frac{1}{9}$ sec., *i. e.* twenty-one vibrations of frequency 192 per second. On different strings the complete change took three times as long. This is due to the vibration of the first string continuing after the bow has left it, so, when the second note begins, which is not for some time after the bow has left the first string, the first note is still sounding, and so distorts the wave due to the second note. Moreover, free vibrations of the string, belly, and diaphragm have to be damped out before the pure forced vibrations of the second string are established. In the first case all these factors are not present, one string giving both notes, there can be no distortion due to the first note persisting after the second is established.

Figs. 17 and 18 show note-changes made by singing. In the first case the change is from a lower note B (480 per sec.) to a higher one D♯ (600 per sec.). In the second case the change is downward from C (512 per sec.) to G (384 per sec.). In both cases the amplitude is seen to fluctuate during the change. The voice moves by small steps from one note to the other, the time taken to establish the second note being in each case about one-fifth of a second. In the case of the violin changing from one note to another there is no sign of slurring between the notes.

Figs. 19 and 20 are traces of portamento from G (768 per sec.) to C (512 per sec.); the first was obtained on the E string of a violin tuned to C, and the second by the human voice. It was thought that the amplitude of the vibration might be a function of the frequency, but response curves plotted between frequencies and amplitudes in the two cases gave entirely different results. In all probability the change of amplitude is partly due to change of intensity in producing the note.

Figs. 21, 22, and 23 are attempted shakes. The first was obtained by the human voice on B (480 per sec.) and C (512 per sec.). Measuring up the curve it was found that ten notes per second were produced, but there was no definition between the successive notes, a slurring from one to the other being noticed as in the cases of jumping from one note to another. Further, the correct frequency of the higher note was not attained every time, being in most cases slightly sharp.

The second and third are bowed notes on the violin, the second being on A (213 per sec.) and B (240 per sec.) on the G string, and the third being on B (480 per sec.) and C (512 per sec.) on the A string. The records show in the case of the lower notes a change from A to B after one-fifth of a second, and a change back to A after one-tenth of a second—but not a quick continuous shake. The higher notes do not give a true shake either, the change in the shape of the curve showing where one note passes to another.

Fig. 24 is a record of a turn sung on C; the notes were intended to be C (512), D (576), C (512), B (480), and C (512 per sec.). According to measurement, there is a longer pause on the lowest note than on the other notes, and the turn is wider than it should be, B♭ being reached.

Fig. 25 is the record of a tremolo sung on $\overline{\text{EE}}$ on C (512) the fluctuation of amplitude being well marked but irregular. The average number of changes of amplitude are about ten per second.

Conclusion.—With the apparatus as at present used, one person must produce the sounds while another exposes a film at the required time. I wish to thank Mr. T. R. Allitt for help in playing the violin and developing the films, and Mr. H. E. Beckett for his help with records of voice and tuning-forks. The author sang all the vocal passages produced in the paper.

Nottingham,
July 15th, 1926.

LXXXVI. *The Joule-Thomson Effect for Air.* *By* N. Eumorfopoulos, *Fellow of University College, London, and* J. Rai, *Lieutenant in the Imperial Japanese Navy* *.

THE experiments of which a description is given below were undertaken with the object of determining the thermodynamic correction to the gas thermometer. They were begun in 1910, but it was not until the early part of 1914 that the most suitable material (alundum) was decided on. Owing to the Great War and other circumstances the experiments were suspended for some years, but taken up again about two years ago. It has been thought preferable to publish them at the present stage, as one of us (J. R.) has been obliged to leave England, although experiments have so far been carried out only at two temperatures, viz., at 20° C. and at 100° C.

---

* Communicated by Prof. A. W. Porter, D.Sc., F.R.S.

The Porous Plug Experiment, as it has been called, consists in forcing gas through a porous plug and measuring the difference of temperature of the gas on the two sides of the plug. In the case of air there is a cooling effect at ordinary temperatures and pressures. Owing to the narrowness of the channels in the plug the increase of the kinetic energy of the gas while passing through them may cause the temperature there to be considerably below that of the gas on either side of the plug. There will thus be a conduction of heat parallel to the direction of flow. This, however, will not alter the temperature of the gas, once the steady state is set up. It is far otherwise with the heat conducted *across* the direction of flow. This quantity must either be allowed for or made negligibly small. Joule and Thomson allowed for it by assuming that it was proportional to the difference of temperature between the issuing gas and the bath in which the plug was immersed, and inversely proportional to the mass of gas flowing in the unit of time. The published statements do not, however, furnish sufficient information as to the exact way in which these subsidiary experiments were carried out. Heating the bath, as Joule and Thomson did, must certainly disturb the distribution of temperature and lead to an erroneous result. To diminish this correction it is necessary to make the plug as thin as possible.

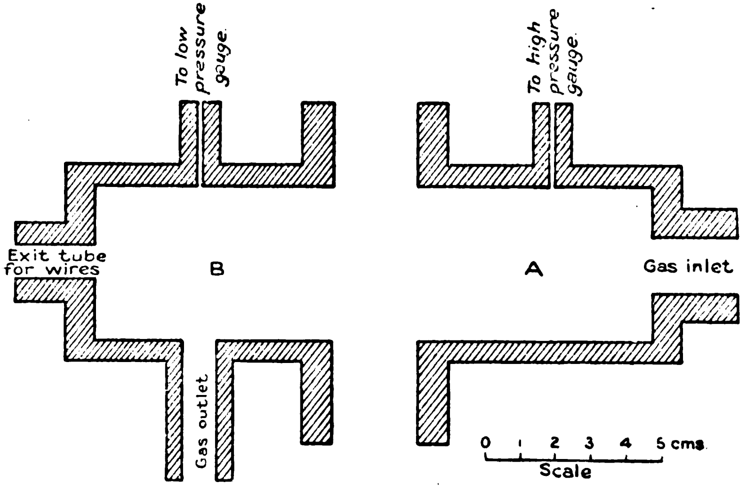
The disturbance caused by the inevitable fluctuations of pressure is, we think, largely diminished by making the thermal capacity of the plug and thermometers as small as possible. For this reason, as well as for others, we have used thermo-electric junctions in preference to platinum thermometers.

DESCRIPTION OF THE APPARATUS.

The apparatus has been designed to measure the Joule-Thomson Effect at the ordinary temperature and at the temperature of boiling liquids. Atmospheric air is dried by passing through layers of soda-lime and calcium chloride and then passes into an electrically-driven water-cooled pump. A by-pass, controlled by a needle-valve, between the inlet and outlet tubes of the pump enables the latter to be worked at a reasonable speed even at low pressures. From the pump the air passes into a reservoir of 25 litres capacity, through a second drying cylinder, and through a U-tube containing cotton-wool. From this last tube the air passes through two heating baths, the first one normally contains oil, while the second one is a vapour-bath. Actual experiment has shown that these two baths are amply sufficient for the largest circulation the pump will give. From the second bath the gas passes directly into a third double-jacketed heater containing the plug-box, the double-jacketing being of the same nature as is used in an ordinary hypsometer. From the plug-box the gas passes through a small U-tube containing cotton-wool, through a water-cooled reservoir of 25 litres capacity, and so back to the pump.

To return to the plug-box. Figure 1 gives a diagrammatic representation of the one used.

Fig. 1.



The plug is cemented in the brass holder shown in fig. 2, which is placed between A and B of fig. 1; A, B, and the plug-holder are then screwed together by bolts passing through the flanges of A and B.

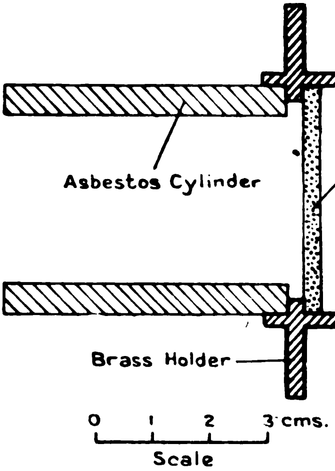
The thermo-electric wires are not shown in the figure.

It will be noticed that in the centre of the plug the gas does not come into contact with any metal with the exception of the thermo-electric wires.

The high-pressure gauge (a Dewrance gauge) can be read to the hundredth part of an atmosphere, and was calibrated at the National Physical Laboratory.

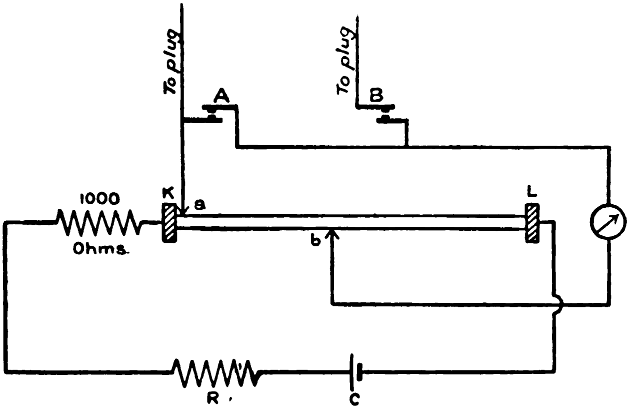
It has already been stated that temperatures were measured with thermo-electric junctions. Three copper-constantan junctions (gauges Nos. 40 and 36 resp.) on each side of the plug are arranged in series, the wires being passed through, and cemented in, the material of the plug itself. The wires project horizontally about 5 cm. into the air space to the right and left of the plug as shown in fig. 2, and are then bent back so as to bring the junctions within a millimetre or two of the surface of the plug. The two copper ends of the junctions pass through a stuffing-box and thence to the potentiometer.

Fig. 2.



The calibrated potentiometer KL consists of two No. 20 manganin wires connected in parallel. On one of these a permanent junction is made (*a* in fig. 3), while the slider *b* is moved on the other until a balance is obtained. The

Fig. 3.



whole arrangement may thus be represented diagrammatically as follows (the Weston cell circuit is omitted) :—

The resistance R is adjustable, while the Weston cell is balanced on the 1000 ohm coil. The two keys A and B are entirely of copper, and enclosed in two asbestos-lagged boxes. Contact is made by screwing down from the outside a wooden screw bearing on ebonite. These keys have been found thoroughly satisfactory. Great care has been taken in insulating the whole circuit from earth currents.

As the temperature of the air passing through the plug does not remain absolutely constant, the following method of observation has been adopted. The key B is closed (A being open), the slider *b* having been already adjusted to the approximately correct balancing-point. Galvanometer readings are then taken at regular intervals for some minutes, the pressure being similarly read, and the means taken. Owing to the temperature variation in the room, there will always be some stray e.m.f. in the circuit. To evaluate this, immediately after the above observations have been taken, B is broken, C is disconnected, and then A is made, the slider remaining untouched. The deflexion so obtained is taken as a measure of the stray e.m.f. The potentiometer zero is obtained by moving the slider *b* to a position opposite *a* with B open and A closed (C being, of course, connected). The stray e.m.f. is measured in this case also. These four measurements are carried out in each observation. The galvanometer sensitiveness (for the interpretation of the meaning of small deflexions) is taken each day. Two measurements of sensitiveness are required—one for the main experiment, and the other for the stray e.m.f., as the resistance of the circuit in the latter case is smaller. Part of the stray e.m.f. arises in the galvanometer itself, and has been much diminished by careful shielding.

It must not be supposed that the pressure fluctuations cause the galvanometer readings to vary to any very large extent, while observations are being made on the Joule-Thomson effect. When one of the thin plugs referred to below is being used, the largest variation in the readings only amounts to some three millimetres of the galvanometer (say ·005 dgr.), even when the pressure difference is small. When a thicker plug is used (Plug No. 3 referred to later), the variations at low pressure differences may be as much as five times the above quantities, but this is a somewhat extreme case.

The thermo-electric e.m.f. of the couple used was determined directly on the potentiometer. The pressure effect on this e.m.f. was tested and found to be negligible for present purposes. The bridge-readings given later can be converted into degrees by multiplying by ·02977 in case of observations at 20° and by ·02570 for observations at 100° C.

THE EXPERIMENTS.

As has already been stated the substance ultimately decided on was alundum, which is made in different porosities, the densest being RA 84. Unless otherwise stated, it is to be understood that the plug used was made of this material and was cemented, in the form of a disk, in the holder shown in fig. 2. It had been hoped that, by making the conduction correction very small, it would be sufficiently accurate to apply the Joule-Thomson method of correction. This accounts for the multiplicity of readings at low pressures. It will be seen that our hope has not been fulfilled.

In the following tables, P_2 indicates the pressure in atmospheres on the high-pressure side of the plug, P_1 that on the low-pressure side, v the volume of air passing through the plug in c.c./sec. measured at the ordinary temperature and pressure (a rough measurement), and L the bridge reading in cms.

Plug No. 3.

This plug is 42 mm. in diameter and 6 mm. thick. The outer portion had been glazed, leaving a central porous portion 25 mm. in diameter. Besides the asbestos tube shown in fig. 2 (which is present in all cases), the protection against conduction of heat consisted of a short glass tube (diam. 27 mm.) cemented on to the disk, and a second one (diam. 15 mm.) within this cutting off a guard-ring.

May 15, 16, 19, & 20, 1924. Observations reduced to 20°C.

P_2.	P_1.	P_2-P_1.	L.	v.
10·93	1·21	9·72	77·31	1470
9·87	1·16	8·71	69·24	1275
8·91	1·15	7·76	62·21	1100
8·06	1·11	6·95	56·18	957
6·89	1·08	5·81	47·21	756
5·98	1·06	4·92	39·95	600
5·03	1·04	3·99	31·63	447
4·05	1·02	3·03	23·10	301
3·00	1·01	1·99	12·24	169
2·04	1·00	1·04	4·21	74
1·70	1·00	0·70	1·98	45
2·98	1·01	1·97	11·88	168
4·72	1·03	3·69	28·59	401
7·08	1·08	6·00	49·25	790
9·20	1·15	8·05	64·96	1153
10·68	1·20	9·48	75·38	1423
7·05	1·08	5·97	48·51	784

These results will be found plotted on diagram 3.

Within the limit of our pressure range the Joule-Thomson effect can be represented by a formula of two terms:

$$a(P_2-P_1)+b(P_2^2-P_1^2).$$

If we could also assume, with Joule and Thomson, that the conduction effect is proportional to the temperature difference and inversely proportional to the quantity of gas flowing in a given time through the plug, then

$$a(P_2-P_1)+b(P_2^2-P_1^2)=L+c\frac{L}{v},$$

where c is some constant. When the formula is applied to the experimental results as is done below, it is found that the value of c is not constant.

It is obvious that, given enough experimental points, a, b, and c can all be determined, and such calculations have been carried out by the method of least squares with all the results communicated in this paper.

With this plug the conduction is somewhat serious. Taking the points up to a pressure difference of 4 atmospheres, the value of c is found to be 115 c.c. If, however, the other ten observations of the above table are used, the value of c is only 49 c.c. This diminution in the value of c as the pressure difference is increased is repeated with all the plugs used, without exception.

February 11 & 12, 1926. Observations reduced to 100° C.

P_2.	P_1.	P_2-P_1.	L.
10·87	1·13	9·74	52·14
10·00	1·11	8·89	47·91
8·97	1·09	7·89	42·95
8·02	1·07	6·95	37·97
7·00	1·05	5·95	32·84
6·00	1·03	4·97	26·79
5·00	1·02	3·98	20·32
4·04	1·01	3·03	13·93
3·07	1·01	2·06	7·20
2·50	1·00	1·50	4·18
1·72	1·00	0·72	0·67

These results will be found plotted on diagram 4.

Plug No. 2.

Disk identical in construction with No. 3, but only 3 mm. thick. Two concentric asbestos-paper tubes, about a cm. in length, were arranged on the low-pressure side, thus cutting off guard-rings.

June 4, 5, & 6, 1924. Observations reduced to 20° C.

P_2.	P_1.	P_2-P_1.	L.	*v*.
10·05	1·23	8·82	70·11	1555
8·86	1·16	7·70	61·18	1317
8·11	1·15	6·96	56·09	1161
7·09	1·12	5·97	47·83	959
5·82	1·08	4·74	37·76	710
4·99	1·06	3·93	31·34	554
3·93	1·03	2·90	22·51	372
2·95	1·01	1·94	13·77	228
1·99	1·00	0·99	5·34	94
1·72	1·00	0·72	3·87	62
3·22	1·01	2·21	15·99	260
4·09	1 03	3·06	24·16	399

These points are plotted on diagram 3.

Calculation of *c* from all points above 3 atmospheres pressure difference gives a value of 36 c.c. On examining diagram 3 it will be found that while for the lowest pressure observed the conduction correction for plug No. 3 is about twice that for plug No. 2, the difference has practically disappeared by the time we get to a pressure difference of 5 atmospheres.

As the plugs just described gave, at low pressures, too high a conduction effect, it was decided to try disks with a thickness of 1 to 2 mm. only. These, if 4 cm. in diameter, would not be strong enough to support a pressure of 10 atmospheres, so a thick alundum ring was cemented in the holder (fig. 2). This ring carried the thermo-electric wires, and was glazed or cemented so as to be non-porous. The inside edge of the ring was bevelled so as to hold securely the disk, which was cemented in place. It will be seen shortly that most of these disks were so porous that a correction has to be made for the kinetic energy of the air on the low-pressure side. It is assumed that no part of this energy is converted into heat on moving past the wires. The correction is occasionally large, and is thus open to some uncertainty.

Plug No. 5.

It was decided to try the effect of different methods of heat insulation. A porous disk of 2 cm. diameter and 1 mm. thickness was fixed as just described. On the low-pressure side an asbestos cylinder of the same diameter was cemented to the plug. As only comparative results were aimed at, the kinetic energy correction, although appreciable, has not been applied. Observations were made on May 28 and June 9, 1925. These will be found plotted on diagram 1.

Asbestos wool was now packed between the two asbestos cylinders. With the plug in this condition observations were made on June 11, which will be found plotted on the same diagram. A small, though noticeable, improvement has been produced in bringing the low-pressure values into line with the high-pressure ones.

After this, a cylinder, about 1 cm. in length and the same in diameter, made of asbestos paper, was fixed on the low-pressure side; the air outside this cylinder was thus made to act as a guard-ring. The observations made on June 22 (see diagram) show that a great improvement has been obtained, which is especially noticeable at low pressures.

In all these cases the junctions were, as has already been stated, within a millimetre or two of the plug. They were now moved about 1 cm. away from the plug on the low-pressure side. This would bring them about level with the opening of the asbestos tube added for the observations on June 22. Results were obtained on June 25 with the plug in the altered condition. From the diagram it will be seen that the last change has produced but a small effect. This experiment shows that with the guard-ring the heat insulation is quite satisfactory, once the gas has passed through the plug.

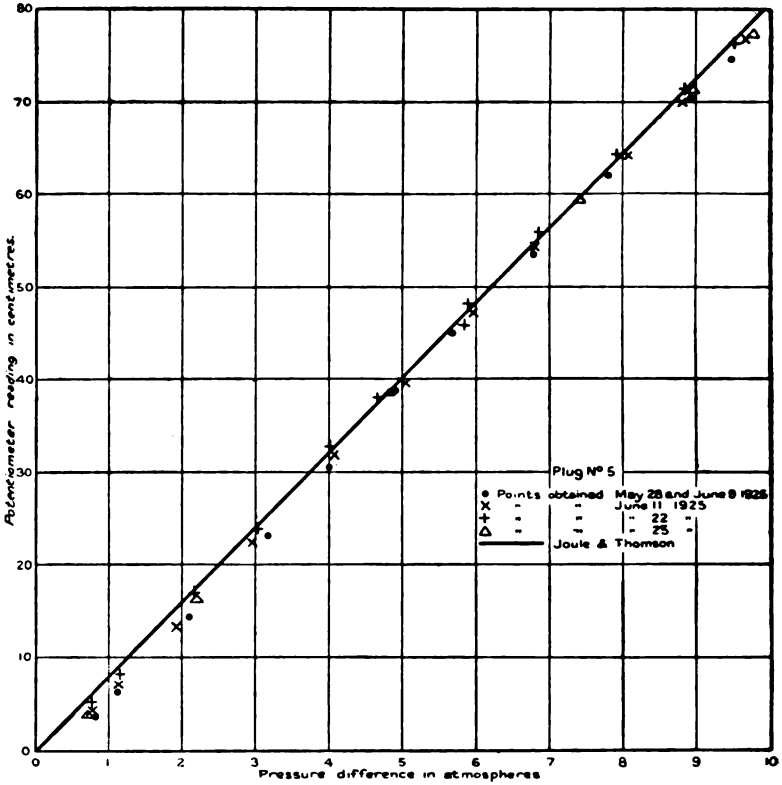
With such a disk the following measurements were taken:—

August 7, 1925. Observations reduced to 20° C.

P_2.	P_1.	P_2-P_1.	L.	v.	L corrected.
10·76	1·17	9·59	75·78	1553	74·85
8·61	1·12	7·49	60·07	1169	59·49
6·89	1·08	5·81	47·01	867	46·66
5·42	1·05	4·37	35·24	609	35·06
3·98	1·03	2·95	23·71	374	23·64
3·20	1·02	2·18	17·07	261	17·03
2·17	1·01	1·16	8·34	122	8·33
1·82	1·00	0·82	5·43	82	5·43
10·68	1·17	9·51	75·74	1540	74·82
9·05	1·13	7·92	63·42	1248	62·77

The last column is the fourth column corrected for kinetic energy as already explained. The above points are indicated on diagram 3. The method of least squares applied to the five lowest points gives for c a value of 19 c.c., while the seven highest give 13·5.

DIAGRAM 1.



August 10 & 11, 1925. Observations reduced to 100° C.

P_2.	P_1.	P_2-P_1.	L.	*v*.	L corrected.
10·76	1·17	9·59	50·62	1453	49·05
8·59	1·11	7·48	40·00	1085	39·03
7·08	1·08	6·00	32·81	825	32·21
5·73	1·05	4·68	25·28	602	24·95
4·07	1·02	3·05	16·23	355	16·11
3·01	1·01	2·00	10·23	213	10·19
2·24	1·01	1·23	5·82	119	5·81
1·84	1·00	0·84	3·55	76	3·54
10·77	1·17	9·60	50·94	1455	49·37
9·67	1·14	8·53	45·60	1267	44·35
8·30	1·10	7·20	38·14	1035	37·24
6·34	1·05	5·29	28·97	704	28·51
5·09	1·04	4·05	21·62	498	21·39
3·48	1·02	2·46	12·91	272	12·84
2·29	1·01	1·28	6·33	125	6·31
1·85	1·00	0·85	3·58	78	3·57
7·77	1·09	6·68	35·90	945	35·14

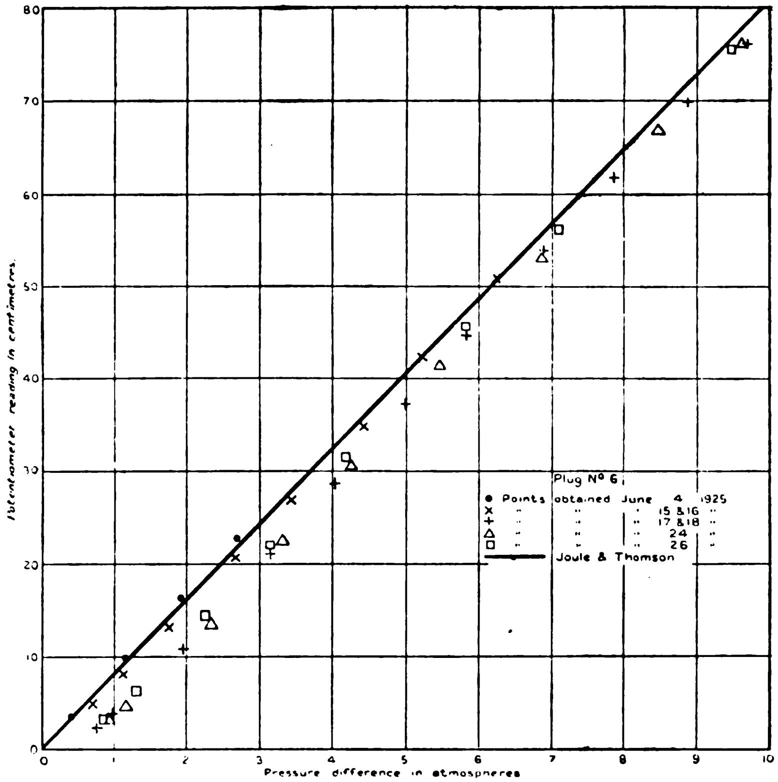
For curve see diagram 4.

The method of least squares applied to the seven lowest points gives for *c* a value of 25 c.c., while the eleven highest give 11·5.

Plug No. 4.

An attempt was made to diminish the conduction effect by supporting the disks on uralite rings cemented to the thick alundum ring. The result is not altogether successful—the favourable effect of the uralite is no doubt neutralized by the additional cement that had to be employed. A somewhat different way of mounting on the uralite might be more successful.

Diagram 2.

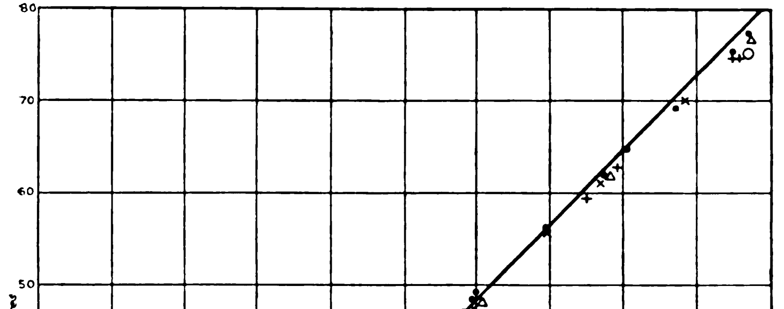


July 28, 1925. Observations reduced to 20° C.

P_2.	P_1.	P_2-P_1.	L.	*v*.	L corrected.
1·78	1·00	0·78	3·23	55	3·23
2·09	1·01	1·08	5·82	82	5·81
3·00	1·01	1·99	13·55	167	13·52
3·90	1·02	2·88	21·48	262	21·42
5·41	1·03	4·38	34·60	445	34·43
7·09	1·05	6·04	48·52	662	48·15
8·88	1·08	7·80	62·52	899	61·85
10·82	1·11	9·71	77·75	1194	76·65
3·48	1·01	2·47	17·90	217	17·86
2·58	1·01	1·57	9·75	126	9·73

These points will be found plotted on diagram 3.

Diagram 3.



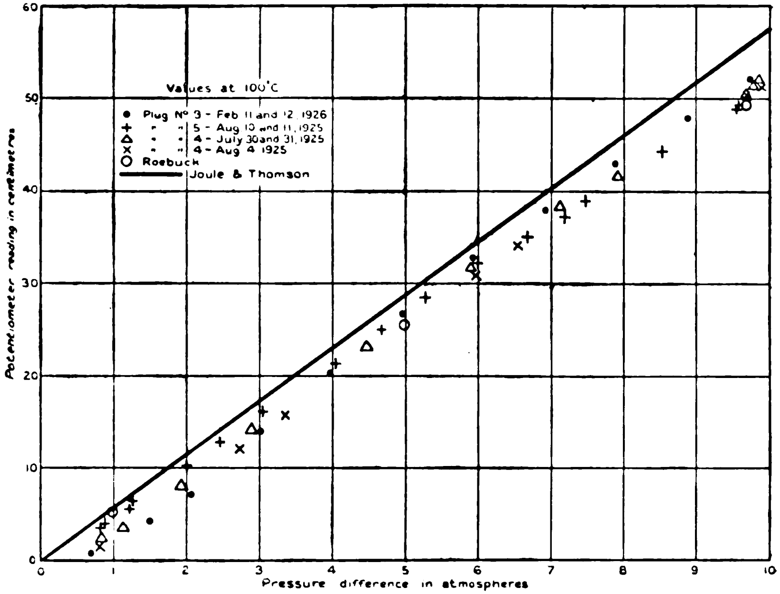
The method of least squares applied to all the points gives for *c* a value of 61 c.c., while, if applied to the six highest points only, we get a value of 48.

July 30 & 31, 1925. Observations reduced to 100° C.

P_2.	P_1.	P_2-P_1.	L.	*v*.	L corrected.
10·78	1·09	9·69	52·11	966	50·71
8·97	1·06	7·91	42·61	753	41·70
6·97	1·04	5·93	32·22	529	31·76
5·50	1·03	4·47	23·50	371	23·27
3·90	1·01	2·89	14·20	216	14·12
2·94	1·01	1·93	8·04	133	8·01
2·14	1·01	1·13	3·83	70	3·82
1·84	1·00	0·84	2·27	47	2·27
10·88	1·10	9·78	52·55	975	51·13
8·18	1·05	7·13	38·87	664	38·16
10·95	1·10	9·85	52·92	984	51·47

These points are plotted on diagram 4. From the eight highest points the value of *c* is 53 c.c.

DIAGRAM 4.



After the above measurements were taken, a little alundum powder was suspended in water; the larger particles were allowed to settle, and then some of the water was passed through the disk so as to diminish the porosity. Experiments carried out on August 4 will be found plotted on the same diagram.

Plug No. 6.

In this case a very porous plug was experimented on, and its porosity diminished by successive additions of fine alundum cement, as in the last case. A disk of RA 225 was accordingly set up (diameter 2 cm., thickness 1·6 mm.) with an asbestos tube 2 cm. in diameter, but no guard-ring. The results will be found plotted on diagram 2. In the observations on June 4, 1925, the highest pressure the pump would give was 4 atmospheres, the low pressure registering 1·31 atm. No kinetic energy correction has been applied.

After a first treatment with alundum powder observations were made on June 15 and 16. After a further treatment with alundum measurements were made on June 17 and 18. On June 24 further readings were taken, after asbestos wool was packed between the two asbestos tubes, and finally on June 26 a guard-ring was placed in position. These values are shown on diagram 2.

DISCUSSION OF THE RESULTS.

On turning to Joule and Thomson's original experiments to see if the conduction correction is satisfactory, we find eight measurements in the neighbourhood of 7°. On reducing these to the same temperature, but before applying the correction under discussion, we find an extreme variation of 4 per cent. This is *increased* to 6 per cent. after the correction is applied, while the highest numbers are those to which the largest correction has been applied (11 or 12 per cent.). The values round about 92° show the same effect, but the numbers are too variable for much stress to be laid on them.

In view of what we have said about the constant diminution of c with increase of pressure, it becomes a question whether, at the high pressures, there is any appreciable conduction correction to apply. On examining the curves in diagram 3 it will be noticed that, however much they may differ initially, they all seem to coincide from a pressure difference of, say, 5 atmospheres upwards. This is confirmed by the results plotted on diagrams 1 and 2. Taking these, as seems justifiable, to give the true values we get the following expression for the Joule-Thomson effect for air at 20° C. (in degrees centigrade):

$$\cdot 2492(P_2 - P_1) - \cdot 0012_8(P_2^2 - P_1^2).$$

Similarly the value at 100° is:

$$\cdot 1453(P_2 - P_1) - \cdot 0009_5(P_2^2 - P_1^2).$$

While this paper was being written, a communication by Roebuck has appeared on the Joule-Thomson effect in air (Proc. Amer. Acad. lx. p. 537). This observer has extended his experiments over a wide range (220 atmospheres and 280° C.). The plug is of the "radial flow" type, *i.e.* it consists of a porcelain tube with one end closed; the gas passes from the outside to the inside of the tube, and the temperatures were measured with encased platinum thermometers. On diagrams 3 and 4 three points are plotted from Roebuck's results. It will be seen that his results are slightly lower than ours. It should be added that Roebuck states that his results for low pressures are not as concordant as those obtained for higher pressures.

In conclusion we wish to tender our best thanks to Mr. J. Rose-Innes, who has borne practically the whole expense of the investigation and has otherwise given us much help. We have also to thank Prof. A. W. Porter, F.R.S., for constant advice and assistance. In the first part of the investigation we had the advantage of help from Mr. J. K. Aykroyd, whose engineering knowledge was of great aid in the designing of the apparatus. To him also we wish to express our indebtedness.

LXXXVII. *On Reversal in Vacuum Tube Spectra.*

By T. R. Merton, *F.R.S.*[*]

THE reversal of the spectrum lines of gases which are excited in vacuum tubes has been observed frequently. This effect is to be expected with tubes in which the light from a constricted portion passes through a long region of larger bore and in which in consequence the excitation is less intense. It is also sometimes observed in the conventional type of end-on tube, in which the capillary opens rather abruptly into a wide tube in which the luminosity is in general very small, but in which one may suppose that there are enough excited atoms to exhibit the phenomenon. This effect has been the subject of several investigations on account of its importance in connexion with secondary standards of wave-length. Perard (*C. R.* clxxvi. p. 375, 1923) has found that in certain sources some of the neon lines appear double or even more complex. Buisson and Jausseran (*C. R.* clxxx. p. 505, 1925) state that this is due to

[*] Communicated by the Author.

reversal, and were unable to observe the effect at right angles to the capillary*. The whole question has recently been discussed by Burns (Journ. Opt. Soc. Amer. xi. No. 4, p. 301, 1925), who concludes that the neon lines are suitable as standards under specified conditions in which the observations are made perpendicular to the capillary. Meissner (*Ann. d. Phys.* lxxvi. p. 124, 1924 ; cf. *Phys. Zeits.* xxvi. p. 687, 1925) has investigated the phenomena of absorption by excited neon, and has found that this is very conspicuous in the case of certain lines which arise from electron transitions terminating in a metastable state. A high resolving power is in general required to observe these reversals directly. I have recently found that this effect can be seen for the D_3 line of helium, not only in long end-on tubes, but also perpendicular to the capillary of a vacuum tube of the conventional pattern if the current density is sufficiently great. The observations were made with an echelon grating having thirty-five plates of glass 15 mm. thick in optical contact, and preliminary analysis was made by means of a constant deviation spectroscope. With an end-on tube about 25 cm. long and of 5 mm. internal bore containing helium at between 5 and 10 mm. pressure the reversal was distinctly seen with quite moderate currents, but it became much more conspicuous when the tube was excited by very heavy currents. The most powerful discharges used were obtained by means of a transformer which raised the voltage of the A.C. supply to 5000 volts, and currents of rather more than 100 milliamperes could be passed through the tube for short periods. With these currents the reversal was very distinct, and appeared to be quite definitely unsymmetrical, the intensity on the more refrangible side of the reversal being somewhat greater. The interpretation of this in so far as the asymmetry is concerned was rendered somewhat uncertain owing to the presence of the fainter component of the D_3 line, since this faint component was not resolved from the next order spectrum of the main line owing to the widths of the lines, the difference in wavelength corresponding to the separation of successive orders being 0·371 Å, whilst the separation of the components is 0·342 Å. There was a distinct broadening of the line at high current densities, but the reversal was very narrow. When the tube was excited by a feeble discharge the reversal could not be seen. It is not at once clear why a heavy discharge should be essential to the observation if the reversal is due to a less strongly excited layer at the end of the capillary, as it would seem that whatever the current through the tube there must be some region at which the conditions for a reversing layer would obtain. An alternative explanation can perhaps be found in the assumption that the apparent reversal is not due to a reversing *layer* at all. We may perhaps suppose that the final state in the transition which gives rise to the D_3 line possesses some measure of metastability, and that atoms remain in this state until they undergo collisions with other atoms. The faster moving atoms are responsible for the emission or absorption at the outer parts of the line, the width of which is due to the components of the velocities of the atoms in the line of sight, and the greater the velocity of an individual atom the shorter will be its expectation of light in a metastable state. The result of this will be that E/A, the ratio of the emissive to the absorptive power, will be a minimum at the centre of the line, since the absorptive power at a particular wave-length depends on the number of atoms in a metastable state which, in virtue of the component of their velocity in the line of sight can absorb that wave-length. An infinite thickness of the gas would thus show a minimum at the centre of the line, and the observation of this minimum in vacuum-tube spectra will depend on a sufficient thickness of the radiating gas, or alternatively on a high current density. It should therefore be possible to observe the phenomenon perpendicular to the capillary of a vacuum tube with very heavy currents, and the experiment was accordingly tried. The tube contained helium at a few millimetres pressure and the internal bore of the capillary was about 2 millimetres. With moderate currents no effect could be seen, but with very heavy currents the reversal was distinctly visible. It was exceedingly narrow, and was indeed just within the resolving power of the echelon, which was over 500,000 in this part of the spectrum, and could not be seen with a small Lummer Gehrcke plate having a nominal resolving power of 200,000.

---

* R. W. Wood (Phil. Mag. x. p. 876, 1926) has recently described the phenomena of reversal in long end-on hydrogen tubes.

The above considerations afford no explanation of the apparent asymmetry, but it is probable that some broadening by the Stark effect is operative at these current densities, and this would cause a widening of the line to the violet, according to the observations of the Stark effect for this line by Takamine and Kokubu (Mem. Coll. Sci. Kyoto, iii. p. 9, 1919). It would seem that it may be necessary to specify the internal bore of vacuum tubes and the current density, when they are to be used as sources of lines for standard wave-lengths.

There is doubtless a layer of less strongly excited gas in the neighbourhood of the walls of any vacuum tube; but the fact that the observation of reversal seems to depend on a high current density appears to imply that the existence of this layer is not sufficient to explain the phenomena.

July 31st, 1926.

LXXXVIII. *On "Relaxation-Oscillations."*

By BALTH. VAN DER POL, Jun., *D.Sc.*[*]

1. THE condition of a simple oscillatory system, possessing one degree of freedom and subjected to a dissipative force, may be represented by the well-known linear differential equation

$$\ddot{x}+\alpha\dot{x}+\omega^2x=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the solution of which is

$$x=C_1e^{-\frac{\alpha t}{2}}\sin\left(\sqrt{\omega^2-\frac{\alpha^2}{4}}\,t+\phi\right). \quad . \quad . \quad . \quad (2)$$

If we have also $\alpha>0$

and $\frac{\alpha^2}{4}<\omega^2$,

the solution (2) represents a damped oscillation with a logarithmic decrement δ given by

$$\frac{\delta}{\pi}=\frac{\alpha}{\omega}.$$

If it happens that the "resistance" in the system is negative, such as may be the case in certain electrical circuits, the sign of α is reversed and (1) becomes

$$\ddot{x}-\alpha\dot{x}+\omega^2x=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the solution of which is

$$x=C_1e^{+\frac{\alpha t}{2}}\sin\left(\sqrt{\omega^2-\frac{\alpha^2}{4}}\,t+\phi\right).$$

If, again, we have $\alpha>0$

and $\frac{\alpha^2}{4}<\omega^2$,

the solution (2 *a*) represents an oscillation; but in this case the amplitude is gradually increasing instead of decreasing, and the logarithmic decrement of the former case is replaced by a logarithmic increment δ given by

---

[*] Communicated by the Author.

$$\frac{\delta}{\pi}=\frac{\alpha}{\omega}.$$

2. A solution of the form (2 *a*) is, however, physically unrealizable because it indicates an amplitude growing to infinity. Thus for actual physical systems the differential equation (3) will only be valid for values of x up to a certain value. To express the limitation of the amplitude we must assume that the coefficient of the "resistance" term is a function of the amplitude itself, becoming positive at the higher values. Thus we may in (3) replace α by the expression $\alpha-3\gamma x^2$, where γ is a constant. Hence we obtain instead of (3):

$$\ddot{x}-(\alpha-3\gamma x^2)\dot{x}+\omega^2 x=0. \quad . \quad . \quad . \quad . \quad (4)$$

This equation has been previously considered * in connexion with the subject of triode oscillations.

Let us now change the units of time and of x and write

$$\left.\begin{aligned} &\omega t=t', \\ \text{and} \qquad &x=\sqrt{\frac{\alpha}{3\gamma}}\,v. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4\,a)$$

Then (4) becomes (after dropping the accents)

$$\frac{d^2v}{dt^2}-\frac{\alpha}{\omega}(1-v^2)\frac{dv}{dt}+v=0. \quad . \quad . \quad . \quad . \quad (5)$$

Writing further

$$\frac{\alpha}{\omega}=\epsilon$$

and using fluxional notation we have

$$\ddot{v}-\epsilon(1-v^2)\dot{v}+v=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Now in the usual cases of triode oscillations we know from the experimental data that it takes several periods for the amplitude to build up to the final steady value. Expressed mathematically this means

$$\epsilon \ll 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

---

* Van der Pol, *Tijdsch . v. h. Ned. Radio Gen.* i. (1920); Radio Review, i. p. 701 (1920). Appleton and van der Pol, Phil. Mag. xliii. p. 177 (1922). Robb, Phil. Mag. xliii. p. 206 (1922).

Recognizing the condition (7) the equation (6) may be solved approximately in the following way:

Let $$v=a\sin(t+\phi),$$

in which, since the logarithmic increment is small, we may assume a to be a slowly varying function of the time, such that

$$\dot{a}\ll a.$$

On substituting (8) in (6), and omitting small quantities and neglecting higher harmonics, we find that

$$\frac{1}{\epsilon}\frac{da^2}{dt}-a^2+\frac{1}{4}a^4=0,$$

or $$a^2=\frac{4}{1+e^{-\epsilon(t+C)}}.$$

The approximate solution of (6) may therefore be written

$$v=\frac{2\sin(t+\phi)}{\sqrt{1+e^{-\epsilon(t+C)}}},$$

which represents an oscillation the amplitude of which at first[*] increases with time according to the factor $e^{\frac{\epsilon t}{2}}$, but finally approaches the steady value

$$a=2.$$

Reverting to the original variables of (4) we thus have

$$x=\sqrt{\frac{\alpha}{\frac{3}{4}\gamma}}\cdot\frac{1}{\sqrt{1+e^{-\alpha(t+C)}}}\cdot\sin(\omega t+\phi). \quad . \quad . \quad (8)$$

There is, however, a more direct method of finding the steady final amplitude of the oscillations for cases represented by (6). For example, let us assume that a periodic solution of the equation exists. Multiplying (6) throughout by $\int v\,dt$ and integrating over the (unknown) period we find that

$$\overline{v^2}=\tfrac{1}{3}\overline{v^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

(the horizontal dashes indicating integration over the period). If now we assume v to be very nearly sinusoidal, *i. e.*

$$v=a\sin t,$$

(9) gives us at once

$$a=2.$$

---

[*] *I. e.*, so long as the amplitude is so small that in (6) the non-linear term $\epsilon v^2\dot{v}$ may be neglected in comparison with $-\epsilon\dot{v}$.

To find the time period of the oscillations we multiply (6) by v and again integrate over the (unknown) period. In this case we find that

$$\overline{\dot{v}^2}=\overline{v^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

so that, assuming again the solution to be approximately sinusoidal, we find from (10), that the angular frequency is unity.

3. Up to the present we have considered (6) with the supplementary condition

$$\epsilon \leqslant 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

but it is of considerable interest, and also the main object of this paper, to investigate the sequence of events when

$$\epsilon \geqslant 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7\,a)$$

It may be noted that even with the new condition (7 *a*) the equation (6) has a periodic solution, since the relations (9) and (10) are independent of the numerical value of ϵ. Further, on physical grounds, we may expect that there is a periodic solution of (6) when (7 *a*) holds, as may be seen from the following considerations. For small values of v, (6) may be written approximately as

$$\ddot{v}-\epsilon\dot{v}+v=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and this has, when (7 *a*) holds, an approximate solution

$$v=C_1e^{\epsilon t}+C_2e^{\frac{t}{\epsilon}}.$$

The value of v therefore would approach infinity asymptotically so that $v=0$ is not a stable solution. Thus, so long as (11) is valid, we are dealing with the well-known *aperiodic* case, but with negative damping. But when the amplitude increases and $v^2>1$, the coefficient of the second term on the left-hand side of (6) becomes positive indicating a positive resistance and therefore a reduction in amplitude with time. Now the limiting values $v=\pm 1$ are not solutions of (6), so that, in general, we may expect the solutions to be periodic, *even when condition* (7 *a*) *is fulfilled*. Although for small amplitudes the resistance has such a big negative value that the linear case would be highly aperiodic, the non-linear term in (6), i. e. $v^2\dot{v}$, makes the solution periodic. We may thus say that we are dealing with a *quasi-aperiodic* solution.

4. It has not been found possible to obtain an approximate analytical solution for (6) with the supplementing

condition (7*a*), but a graphical solution may easily be found in the following way. If we write

$$\dot{v}=z,$$

(6) may be written

$$\frac{dz}{dv}-\epsilon(1-v^2)+\frac{v}{z}=0, \quad . \quad . \quad . \quad . \quad (12)$$

which is a first order equation of the super-Riccatti type. Let us draw in a z, v plane a series of "isoclynes," *i. e.* curves connecting all points for which $\frac{dz}{dv}$ is equal to a certain quantity. An example of such isoclynes is denoted by

$$\frac{dz}{dv}=C_1$$

where C_1 is a constant so that, combining with (12), we have as expression for an isoclyne:

$$C_1-\epsilon(1-v^2)+\frac{v}{z}=0.$$

Several of these isoclynes may be drawn in the z, v plane, and we can indicate by means of short lines, as is done in fig. 1, the direction the integral curve must have when it crosses an isoclyne. (For example, this direction for the isoclyne C_1 is given by

$$\frac{dz}{dz}=C_1, \text{ etc.})$$

From a diagram in which the inclinations of the integral curves are marked on the isoclynes we may easily draw the integral curves in the z, v plane. This is done in fig. 1 for the value

$$\epsilon=0{\cdot}1,$$

and it is seen that the integral curve obtained indicates the track of a point approaching a closed curve after many complete circuits (small increment).

In the same way fig. 2 is drawn for

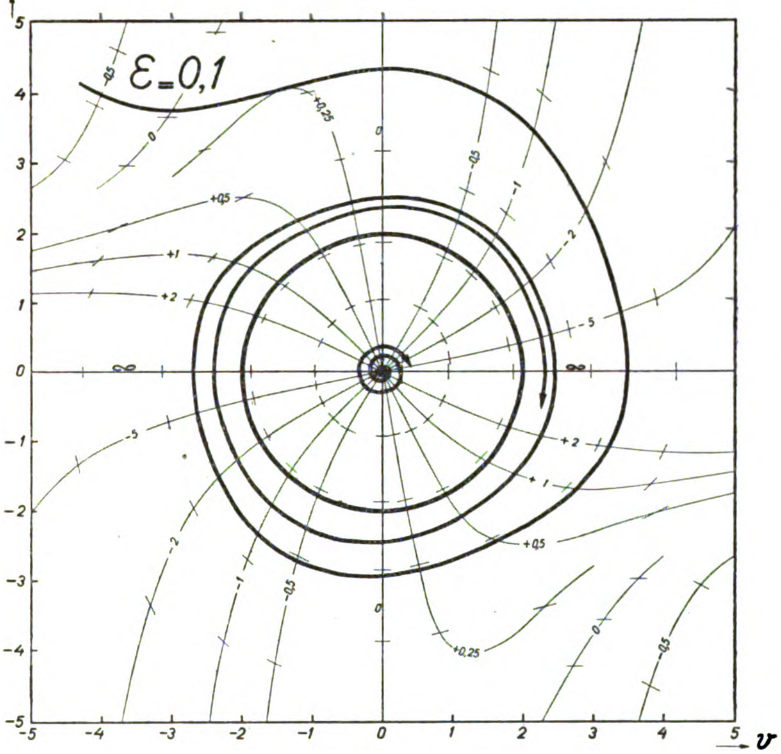
$$\epsilon=1,$$

and fig. 3 for

$$\epsilon=10,$$

all three figures showing a closed curve solution. In the

Fig. 1.



case of fig. 3 (quasi-aperiodic case) the final steady closed curve, representing the periodic solution, is practically reached after one revolution only. When the intermediate integral $z=f(v)$ has been obtained in this way it is easy to construct from it in a similar fashion the integral

$$v=\phi(t).$$

Some examples of such results are exhibited in fig. 4 and represent the solution of (6) for the three cases

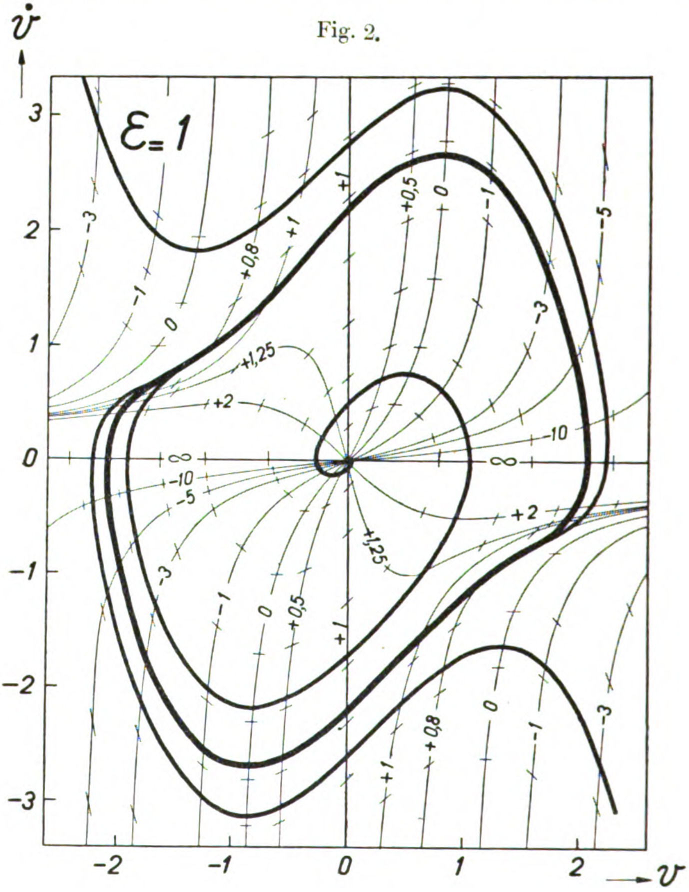
$$\epsilon=0{\cdot}1,$$

$$\epsilon=1,$$

$$\epsilon=10.$$

The first case (small increment) might also have been plotted from the solution (8), and a numerical comparison of the two solutions shows them to be in satisfactory agreement. This case represents a sinusoidal oscillation of gradually increasing amplitude, the value of which is finally

Fig. 2.



steady and equal to 2. The angular frequency, for the units used, is unity. The second case of fig. 4, (i. e. $\epsilon = 1$) indicates a somewhat similar sequence of events, but here the final amplitude is reached in fewer oscillations, while a marked departure from the sinusoidal form is noticed. The third case (i. e. $\epsilon = 10$) is particularly interesting. Here it is noticed that the curve first rises asymptotically and after

Fig. 3.

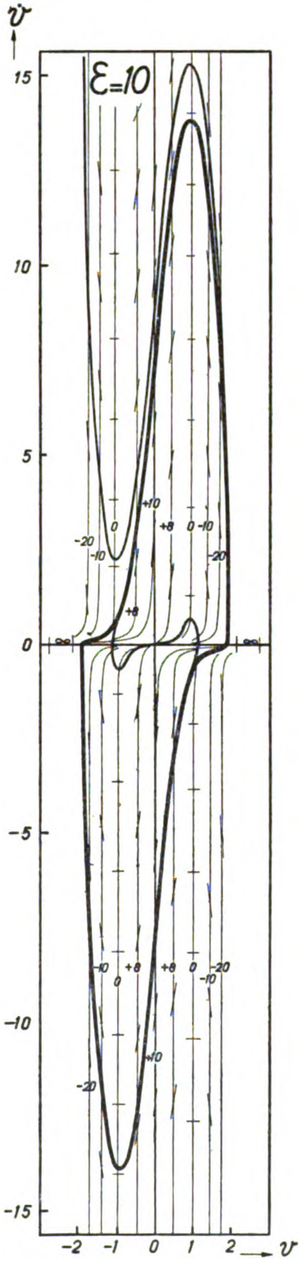
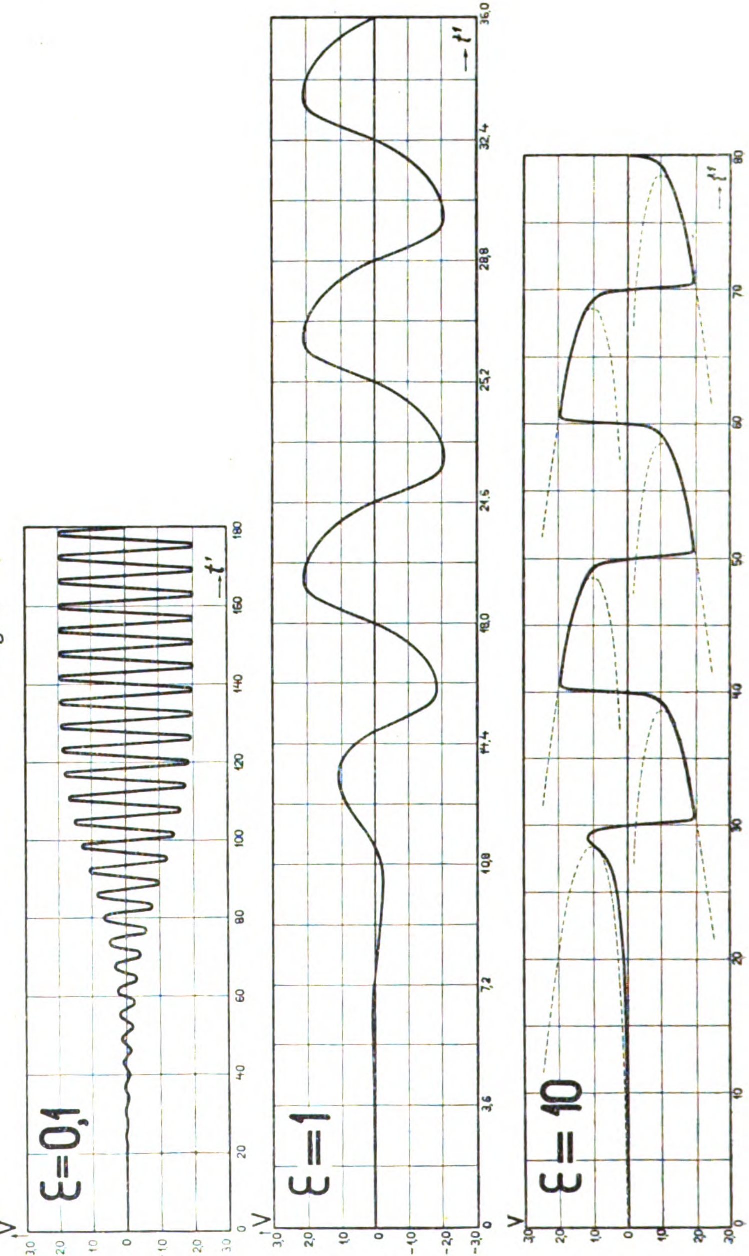

$\dot{v}$
$\varepsilon = 10$
15
10
5
0
−5
−10
−15
−2
−1
0
1
2
v
∞
∞
+10
0
+8
0
−10
−20
−10
−20
+8
−10
+8
0
+8
0
−20
−10
+10
−20

Fig. 4.


ε=0,1
V
3,0
2,0
1,0
0
-1,0
-2,0
-3,0
0
20
40
60
80
100
120
140
160
180
t'
ε=1
V
3,0
2,0
1,0
0
-1,0
-2,0
-3,0
0
3,6
7,2
10,8
14,4
18,0
21,6
25,2
28,8
32,4
36,0
t'
ε=10
V
3,0
2,0
1,0
0
1,0
2,0
3,0
0
10
20
30
40
50
60
70
80
t'

only one period practically reaches the final steady state. This steady state is characterized by a very marked departure from the sinusoidal form. It is seen that the amplitude alters very slowly from the value 2 to the value 1 and then very suddenly it drops to the value -2. Next we observe a very gradual increase from the value -2 to the value -1 and again a sudden jump to the value 2. This cycle term proceeds indefinitely.

Obviously this form of oscillation contains many higher harmonics of considerable amplitude. As will be seen later, the period T, instead of being 2π (as was the case when $\epsilon \ll 1$) increases with increase of ϵ, and when $\epsilon \gg 1$ becomes equal to approximately ϵ itself; that is, we have

$$T \doteqdot \epsilon.$$

Let us now consider more closely the physical factors determining the value of the period T. If our equation (1) represents the circulation of electricity in a system of resistance R, capacity C, and inductance L, we have, as usual,

$$\alpha = \frac{R}{L},$$

$$\omega^2 = \frac{1}{LC}.$$

Now for the time period expressed in units of t' we have already

$$T \doteqdot \epsilon,$$

so that, expressed in terms of t, the period becomes

$$T = \frac{\alpha}{\omega^2} = RC, \quad \ldots\ldots \quad (13)$$

which is a *time of relaxation* (time constant).

Thus our equation (6) for the quasi-aperiodic case, which differs considerably from the normal approximately sinusoidal solution, has again a purely periodic solution, the time period of which is expressed by the time of relaxation of the system. For this reason the term *relaxation-oscillation* is suggested for this phenomenon.

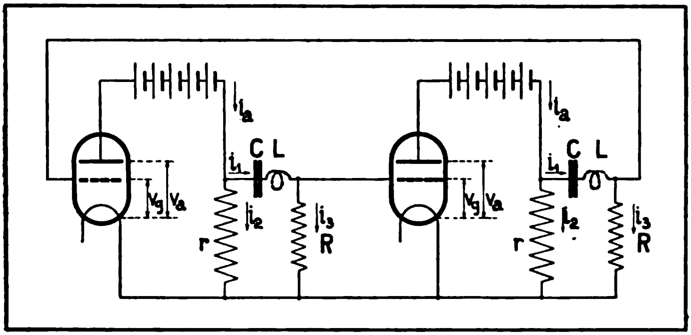
5. A type of oscillation previously described by Abraham & Bloch* is an example of relaxation-oscillations. These authors used an electrical system comprising two triodes and resistances and capacities only, which system

---

* Abraham & Bloch, *Ann. de Physique*, xii. p. 237 (1919).

they called "multivibrateur" because of the many higher harmonics of appreciable amplitude which it produced when oscillating. This system, which may be regarded as a two-stage resistance-capacity coupled amplifier with the output coupled back to the input side, is shown in a slightly modified form in fig. 5. In their original description of the system Abraham & Bloch draw attention to the fact that the time period of the oscillations produced by the multivibrator is approximately equal to the product RC (see fig. 5), but, so far as I am aware, no theoretical discussion of the way in which the oscillations are *maintained* has been published.

Fig. 5.



From the symmetrical value of the circuit we may expect that the two triodes can vibrate in exactly opposite phases. It is further known that the potentials and anode currents experience temporal variations closely represented by fig. 4 ($\epsilon = 10$). Now, in order to explain the reason for the maintenance of oscillation in this system containing resistances and capacities only, we found it necessary to take into account the inductance L of the wires connected to the two capacities. (These are represented by the dotted lines L in fig. 5.) With the notation of the latter figure the current and potential departures from the unstable equilibrium values are given by the following equation :

$$\left.\begin{aligned} -v_{a1}=r_1 i_1 &= \left(R+L\frac{d}{dt}+\frac{1}{C}\int dt\right)i_3 \\ Ri_3 &= -v_{g2} \\ i_{a1}=i_1+i_3 &= \phi(v_{g1}), \end{aligned}\right\} \quad . \quad . \quad . \qquad (14)$$

where $\phi(v_{g1})$ denotes the characteristic of the first triode round the equilibrium position and where, for simplicity, the influence of the anode potential on the anode current is neglected. Further, assuming that the triodes of this symmetrical system are exactly equal and vibrate in opposite phase, we have

$$v_{g1}=-v_{g2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

From (14) and (15) we derive

$$\left(L\frac{d}{dt}+(R+r)+\frac{1}{C}\int dt\right)v_{g1}=Rr\phi(v_{g1}). \quad . \quad (16)$$

Now, as an approximate expression for the characteristic

$$i_{a1}=\phi(v_{g1}),$$

we may take again the third order parabola

$$i_{a1}=S\left(1-\frac{v_{g1}^2}{v_{g0}^2}\right)v_{g1}, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where S is the slope of the anode-current/grid-voltage curve.

Usually the anode lead resistance r is small compared with the grid leak R, *i. e.*

$$r \ll R,$$

so that from (16) and (17) we have

$$L\ddot{v}_{g1}-R\left\{(rS-1)-rS\frac{v_{g1}^2}{v_{g0}^2}\right\}\dot{v}_{g1}+\frac{1}{C}v_{g1}=0. \quad (18)$$

From (18) we note that the "resistance" of the system for small amplitudes is only negative so long as

$$rS>1,$$

so that we have here the approximate condition for the production of oscillations. If we further make the following substitution :

$$\left.\begin{aligned} t&=t'\sqrt{CL} \\ \frac{v_{g1}}{v_{g0}}&=v\sqrt{\frac{rS-1}{rS}} \\ \epsilon&=R(rS-1)\sqrt{\frac{C}{L}} \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

(18) may be written

$$\ddot{v}-\epsilon(1-v^2)\dot{v}+v=0, \quad . \quad . \quad . \quad (6)$$

which is the equation originally discussed and which may be said to be the representative differential equation of the multivibrator ($\epsilon \gg 1$). But we may note that, in order to represent the action of the multivibrator by this equation, we had to take into account the small inductance L of the wires connected to the capacities C, as shown in fig. 5.

We further note from (19) that ϵ depends on the value of $L^{-\frac{1}{2}}$ so that ϵ increases without limit the further L is decreased. We may make a rough estimate of ϵ for the following practical values :

$$R=10^5 \text{ ohms}, \quad rS-1=3, \quad C=0\cdot01\ \mu\text{fd}, \quad L=10 \text{ cm}.$$

In this case,

$$\epsilon=10^5 . 3 . \sqrt{\frac{10^{-8}}{10^{-8}}}=3 . 10^5,$$

so that the conduction

$$\epsilon \gg 1$$

is certainly satisfied. The smaller the value of the residual inductance L, the greater is this inequality.

It therefore may be concluded that the special vibration of the multivibrator represents an example of a general type of relaxation-oscillations and that in order to explain the maintenance of the oscillations we have to take into account the residual inductance of the system (as shown in fig. 5), *however small this may be.*

The result of the above discussion illustrates how the form of the solution of differential equations like the representative equal (18) or (6) is entirely altered by taking into account a term with an infinitesimal coefficient (*e. g.* the first term $L\ddot{v}_{g1}$ in (18)).

But the physical reason for taking this into account becomes immediately apparent when we solve (18) or (6) omitting the first term. In this case the solution of (6) is

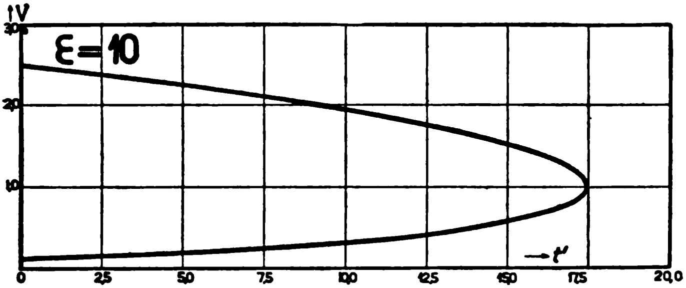
$$\log v^2 - v^2 = \frac{2t+C}{\epsilon}, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

which is represented graphically in fig. 6. We note that the value of v^2 first increases exponentially with time, but near $v^2=1$ the curve bends upwards with an infinite slope, there being further no solution in the real domain. When the inductance is thus disregarded both $\dot{v}$ and $\ddot{v}$ become infinite when $v=\pm 1$, so that the condensers C (fig. 5) would acquire a very large charge in an indefinitely small time. But these infinitely sudden changes of current are prevented by the presence of the small residual inductance.

This is illustrated by the fact that the solution (20) for the derivation of which the inductance has been neglected, and which is represented by the repeated dotted lines in fig. 4 ($\epsilon = 10$), is found to coincide approximately with the exact solution so long as the slope of v is small. Whenever, however, the slope tends to become infinite we note that the term $\ddot{v}$ in (6) becomes of importance and keeping the slope finite maintains the multivibrator in vibration.

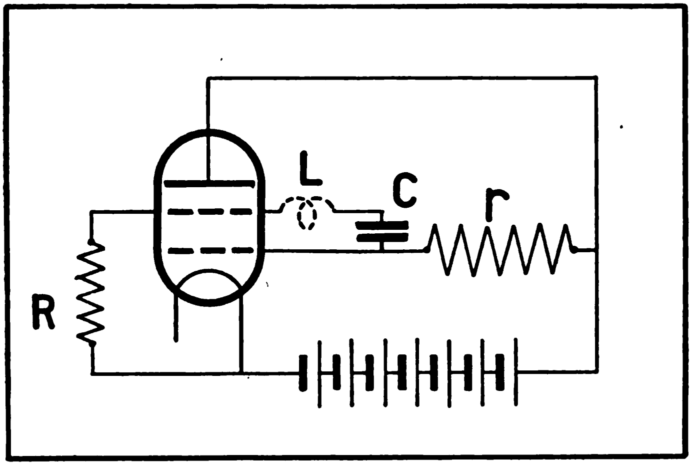
The multivibrator may therefore be compared to a double steam engine with a flywheel which is much too small. The small inertia of the flywheel must, however, be present to carry the system beyond its equilibrium (dead) points.

Fig. 6.



6. Now that the general equation (4) for *relaxation-oscillations* is known, it is an easy matter to devise further electrical systems of the same type. One such a system is depicted in fig. 7 and comprises a tetrode, two resistances r and R, and a condenser C. If we again recognize the

Fig. 7.



inductance L of the wire connecting the condenser to the outer grid, we find that the circulation of electricity in the system is represented by (6). An experimental test of the system showed that the system produced oscillations with a time period approximately equal to CR. When r is replaced by a telephone receiver the oscillations become audible and the change of frequency by changing R or C is easily demonstrated.

7. Finally it seems quite likely that, when the total characteristic (including the parts with a negative slope) is taken into account, the well-known vibration of a neon-tube connected to a resistance and condenser in shunt * may be similarly treated under the heading of relaxation-oscillations.

Similarly, (though no detailed investigation has been carried out) it is likely that the oscillations of a "Wehnelt" interrupter belong to the general class of relaxation-oscillations and perhaps also heart-beats.

Eindhoven, 6th May, 1926.
Physical Laboratory,
Philips' Glowlampworks, Ltd.

LXXXIX. *The Crystalline Structure of Anhydrite.*
By Prof. Jarl A. Wasastjerna †.

IN a particularly interesting paper published in the July number of this Journal, Messrs. Dickson and Binks examined the structure of Anhydrite. In a note added, it is stated that the present author had previously examined the same problem (*Societas Scientiarum Fennica : Commentationes Physico-Mathematicæ*, ii. p. 26, 1925), and that the two investigations produced structures of the same type but of somewhat different parameter values. From that the conclusion might be drawn, that the two pieces of work stand in certain opposition to each other, if only in detail. But that can hardly be said to be the case.

By virtue of a method of elimination, carried through tently, which takes every type of structure, mathe-ly possible, into consideration (in this case there are lifferent types), the present author has shown that of anhydrite there are two, and only two,

---

llreuter, 'Ueber Schwingungserscheinungen in Entlad-
nschweig, 1923.
by Prof. W. L. Bragg, F.R.S.

possible structures. In the present author's work these structures are denoted as IV and V (pp. 39–40). Let us call them A and B. These two structures are of the same type and extremely closely related to one another. A displacement of the atom groups in the direction of the a-axis of 0·05 transforms one structure to the other.

The atomic coordinates are :—

$$\mathrm{Ca}:\left\{\begin{array}{ll} [[q\cdot\frac{1}{4}\cdot 0]] & [[\bar{q}\cdot\frac{3}{4}\cdot 0]] \\ [[q+\frac{1}{2}\cdot\frac{1}{4}\cdot\frac{1}{2}]] & [[\bar{q}+\frac{1}{2}\cdot\frac{3}{4}\cdot\frac{1}{2}]] \end{array}\right.$$

$$\mathrm{S}:\left\{\begin{array}{ll} [[r\cdot\frac{1}{4}\cdot 0]] & [[\bar{r}\cdot\frac{3}{4}\cdot 0]] \\ [[r+\frac{1}{2}\cdot\frac{1}{4}\cdot\frac{1}{2}]] & [[\bar{r}+\frac{1}{2}\cdot\frac{3}{4}\cdot\frac{1}{2}]] \end{array}\right.$$

$$\mathrm{O}:\left\{\begin{array}{ll} [[f\cdot g\cdot 0]] & [[\bar{f}\cdot g+\frac{1}{2}\cdot 0]] \\ [[f\cdot\bar{g}+\frac{1}{2}\cdot 0]] & [[\bar{f}\cdot\bar{g}\cdot 0]] \\ [[f+\frac{1}{2}\cdot g\cdot\frac{1}{2}]] & [[\bar{f}+\frac{1}{2}\cdot g+\frac{1}{2}\cdot\frac{1}{2}]] \\ [[f+\frac{1}{2}\cdot\bar{g}+\frac{1}{2}\cdot\frac{1}{2}]] & [[\bar{f}+\frac{1}{2}\cdot\bar{g}\cdot\frac{1}{2}]] \\ [[h\cdot\frac{1}{4}\cdot k]] & [[\bar{h}\cdot\frac{3}{4}\cdot\bar{k}]] \\ [[h\cdot\frac{1}{4}\cdot\bar{k}]] & [[\bar{h}\cdot\frac{3}{4}\cdot k]] \\ [[h+\frac{1}{2}\cdot\frac{1}{4}\cdot k+\frac{1}{2}]] & [[\bar{h}+\frac{1}{2}\cdot\frac{3}{4}\cdot\bar{k}+\frac{1}{2}]] \\ [[h+\frac{1}{2}\cdot\frac{1}{4}\cdot\bar{k}+\frac{1}{2}]] & [[\bar{h}+\frac{1}{2}\cdot\frac{3}{4}\cdot k+\frac{1}{2}]] \end{array}\right.$$

We introduce the following new parameters :—

$$\begin{aligned} f&=r+t_1 \\ g&=\tfrac{1}{4}-u_1 \\ h&=r-t_2 \\ k&=u_2. \end{aligned}$$

The parameters acquire the following values according to Messrs. Dickson and Binks and to the present author :—

Wasastjerna.	Dickson and Binks *.
$t_1=0{\cdot}16$	$t_1=0{\cdot}15$
$t_2=0{\cdot}16$	$t_2=0{\cdot}15$
$u_1=0{\cdot}19$	$u_1=0{\cdot}18$
$u_2=0{\cdot}19$	$u_2=0{\cdot}18$
$q=\frac{1}{2}+r$	$q=\frac{1}{2}+r$

Alternative A.	Alternative B.
$r=0{\cdot}10$	$r=0{\cdot}15$

It should be emphasized that r cannot have values in the

---

* In Messrs. Dickson and Binks' work another system of notation is used. In our calculation the final results have been shortened so that all the parameters are given in two decimals only.

neighbourhood of 0·12–0·13, *i. e.* the value must be either 0·10 or 0·15. There can be no further alternative.

The choice between the alternatives A and B is difficult. While the present author preferred the alternative B, *Dickson and Binks' parameter values show themselves to correspond to the alternative A*. As to the choice between these alternatives the present author does not positively maintain his earlier opinion, which was principally dictated by the fact that the alternative A for the reflexion (210) leads to an intensity, theoretically calculated, which does not satisfactorily agree with experiments. Messrs. Dickson and Binks have found the same difference in the reflexion (210), but nevertheless held to structure A, since structure B, as Mr. Dickson kindly informed the present author, shows defective agreement with the spectrometrically measured reflexions (202), (220), and (440). In the powder photographs examined by the present author, the reflexions (202) and (220) coincide. The reflexion (440) falls outside the ground observed

---

XC. *On Equilibrium and Motion of a Continuous Medium in Four-dimensional Space. By* D. MEKSYN [*].

§ I. *Introduction.*

IN the present paper we apply the laws of four-dimensional space to a continuous medium (see D. Meksyn, Phil. Mag. Dec. 1925, p. 1227).

Deriving the equation of continuity and the general conditions of equilibrium and motion of such a medium, we accept it as the dynamical laws of an electromagnetic field.

The main results, which are obtained from these considerations, are :—

1. The transformation of mechanical forces in electrodynamics is a particular case of transformation of volume forces in such medium.

2. Radiation of an electron in continuous motion is incompatible with the mechanical equilibrium of the electromagnetic field.

3. In connexion with this we show that a discontinuous change of velocity of a material point (electron) is accompanied by heat generation.

---

[*] Communicated by Mr. F. S. Spiers, O.B.E., B.Sc.

I. THE GENERAL LAWS OF EQUILIBRIUM AND OF MOTION.

§ 2. *The Law of Continuity.*

Take a continuous medium at rest relative to an observer. The law of continuity of such medium in three-dimensional space is

$$\rho\, dx\, dy\, dz = \text{const.}$$

According to our assumption, motion of the three-dimensional space is equivalent to change of position in four-dimensional space-time continuum. Hence we take as the law of continuity in motion

$$\rho\, dx\, dy\, dz\, dl = \text{const.}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or $$\iiiint \rho_1\, dx_1\, dy_1\, dz_1\, dl_1 - \iiiint \rho\, dx\, dy\, dz\, dl = 0.$$

Denoting:

$$D = \begin{vmatrix} \frac{\partial x_1}{\partial x}, & \frac{\partial x_1}{\partial y}, & \frac{\partial x_1}{\partial z}, & \frac{\partial x_1}{\partial l} \\ \frac{\partial y_1}{\partial x}, & \frac{\partial y_1}{\partial y}, & \frac{\partial y_1}{\partial z}, & \frac{\partial y_1}{\partial l} \\ \frac{\partial z_1}{\partial x}, & \frac{\partial z_1}{\partial y}, & \frac{\partial z_1}{\partial z}, & \frac{\partial z_1}{\partial l} \\ \frac{\partial l_1}{\partial x}, & \frac{\partial l_1}{\partial y}, & \frac{\partial l_1}{\partial z}, & \frac{\partial l_1}{\partial l} \end{vmatrix}, \quad . \quad . \quad . \quad . \quad (2)$$

we obtain according to the well-known formula of transformation of coordinates:

$$\rho_1 D = \rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

To transform (2), we have

$$x_1 = x + dx = x + \frac{dx}{d\tau} d\tau \; . \; . \; . \; . \; . \quad l_1 = l + \frac{dl}{d\tau} d\tau,$$

where $$d\tau^2 = dx^2 + dy^2 + dz^2 + dl^2.$$

Denoting:

$$\frac{\partial x}{\partial \tau} = q_x, \quad \frac{dy}{d\tau} = q_y \; . \; . \; . \quad \frac{dl}{d\tau} = q_l, \quad . \quad . \quad . \quad (4)$$

we have instead of (2)

$$D = \begin{vmatrix} 1 + \frac{\partial}{\partial x}(q_x d\tau), & \frac{\partial (q_x d\tau)}{\partial y}, & \frac{\partial (q_x d\tau)}{\partial z}, & \frac{\partial (q_x d\tau)}{\partial l} \\ \frac{\partial (q_y d\tau)}{\partial x}, & 1 + \frac{\partial (q_y d\tau)}{\partial y}, & \frac{\partial (q_y d\tau)}{\partial z}, & \frac{\partial (q_y d\tau)}{\partial l} \\ \cdot \quad \cdot \quad \cdot & \cdot \quad \cdot \quad \cdot & \cdot \quad \cdot \quad \cdot & \cdot \quad \cdot \quad \cdot \\ \frac{\partial (q_l d\tau)}{\partial x}, & \frac{\partial (q_l d\tau)}{\partial y}, & \frac{\partial (q_l d\tau)}{\partial z}, & 1 + \frac{\partial}{\partial l}(q_l d\tau) \end{vmatrix}. \quad (5)$$

Neglecting infinitely small quantities of higher order, we obtain from (3) and (5)

$$\rho_1 \left\{ 1 + \frac{\partial}{\partial x}(q_x d\tau) + \frac{\partial}{\partial y}(q_y d\tau) + \frac{\partial}{\partial z}(q_z d\tau) + \frac{\partial}{\partial l}(q_l d\tau) \right\} = \rho.$$

Hence

$$\rho_1 - \rho + \frac{\partial q_x}{\partial x} d\tau + \frac{\partial q_y}{\partial y} d\tau + \frac{\partial q_z}{\partial z} d\tau + \frac{\partial q_l}{\partial l} d\tau$$

$$+ \left\{ \frac{\partial d\tau}{\partial x} q_x + \frac{\partial d\tau}{\partial y} q_y + \frac{\partial d\tau}{\partial z} q_z + \frac{\partial d\tau}{\partial l} q_l \right\} = 0. \qquad (6)$$

The expression in brackets vanishes and (6) becomes after easy transformations:

$$\frac{\partial}{\partial x}(\rho q_x) + \frac{\partial}{\partial y}(\rho q_y) + \frac{\partial}{\partial z}(\rho q_z) + \frac{\partial}{\partial l}(\rho q_l) = 0, \quad . \quad (7)$$

the equation of continuity accepted in the Theory of Relativity.

This representation of the law of continuity brings out the meaning of Minkowsky's well-known geometric construction in 'Raum und Zeit,' which has to explain the change of dimensions of bodies (space) in motion.

As we see, *it illustrates only the law of continuity of a fluid in motion, and not the properties of space and time.*

§ 3. *Transformation of Forces.*

Consider how volume forces are transformed which arise in a continuous medium and are transmitted by such medium.

Let F′(X′, Y′...L′) be a force on a unit of "mass" (or unit of volume if ρ=const.) of our medium at a system M′ and F(X, Y...L) the corresponding force in another system M in relative uniform rectilinear motion.

We assume that the force is due to a displacement of the medium.

According to the law of continuity,

$$\rho' \mathrm{F}' dx' dy' dz' dl' = \rho \mathrm{F} \, dx \, dy \, dz \, dl,$$

or for the summary forces:

$$\rho' \mathrm{F}' dx' dy' dz' = \mathbf{K}' \quad \text{and} \quad \rho \mathrm{F} \, dx \, dy \, dz = \mathbf{K},$$

we obtain

$$\mathbf{K}' \frac{dt'}{dt} = \mathbf{K} \quad \text{or} \quad \mathbf{K}' \sqrt{1 - v^2} = \mathbf{K}. \quad . \quad . \quad . \quad (8)$$

We see that the force is transformed not as a vector, but gets an additional factor, which is the result of the law of continuity of the medium.

This explains the somewhat uncommon transformation of mechanical forces in electrodynamics.

§ 4. *Statics.*

On each element of a continuous medium volume and surface forces can act. At the basis of statics, as in the classical mechanics, we equate to zero the sum of projections of all forces upon the four axes, and the sum of momenta upon six coordinate planes; in all ten equations:

As Epstein has shown (*Ann. d. Phys.* 1911, p. 36) in case of a stationary system we derive from the six equations of momenta the six equations of equilibrium of classical mechanics.

Hence the conditions of equilibrium are

$$\Sigma \mathbf{K}'=0, \quad \Sigma[r'\mathbf{K}']=0. \quad . \quad . \quad . \quad . \quad (9)$$

If this system is set in motion, the forces considered from a stationary system become

$$\mathbf{K}=\sqrt{1-v^2}\mathbf{K}',$$

and the "lengths" $r=r'$.

Hence
$$\Sigma\mathbf{K}=\sqrt{1-v^2}\Sigma\mathbf{K}=0,$$
$$\Sigma[r\mathbf{K}]=\sqrt{1-v^2}\Sigma[r'\mathbf{K}']=0,$$

or if the medium is in equilibrium in one system of reference it remains in equilibrium in every other in relative uniform rectilinear motion.

§ 5. Let ρ be the "density" of the medium. The conditions of equilibrium are the following ten equations:

$$\left.\begin{array}{l} \iiiint \rho \mathrm{X}\,dv+\iiint \mathrm{T}_x d\sigma=0, \\ \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \iiiint \rho(y\mathrm{Z}-z\mathrm{Y})dv+\iiint(y\mathrm{T}_z-z\mathrm{T}_y)d\sigma=0, \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \end{array}\right\}, \quad . \quad (10)$$

where X, Y, Z, L; T_x, T_y, T_z, T_L are respectively volume and surface forces, dv and $d\sigma$ are elements of four-dimensional volume and three-dimensional surface.

Using the same method as the classical mechanics, that is, considering the equilibrium of an elementary pentahedron in four-dimensional space, and denoting

$$T=\left|\begin{array}{cccc} T_{xx}, & T_{xy}, & T_{xz}, & T_{xl} \\ T_{yx}, & T_{yy}, & T_{yz}, & T_{yl} \\ T_{zx}, & T_{zy}, & T_{zz}, & T_{zl} \\ T_{lx}, & T_{ly}, & T_{lz}, & T_{ll} \end{array}\right|, \quad . \; . \; . \; . \quad (11)$$

we obtain:

$$\left.\begin{array}{l} T_x = T_{xx}\cos\alpha + T_{xy}\cos\beta + T_{xz}\cos\gamma + T_{xl}\cos\delta, \\ . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \end{array}\right\} \quad (12)$$

where $\cos\alpha = \frac{dx}{d\tau}, \quad \cos\beta = \frac{dy}{d\tau} \ldots,$

and $d\tau^2 = dx^2 + dy^2 + dz^2 + d\tau^2.$

Inserting (12) in the first four equations of (10), and transforming, according to Gauss' theorem, the surface integrals into volume, we obtain the four equations of equilibrium:

$$\left.\begin{array}{l} \rho X + \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} + \frac{\partial T_{xl}}{\partial l} = 0, \\ \rho Y + \frac{\partial T_{yx}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial T_{yz}}{\partial z} + \frac{\partial T_{yl}}{\partial l} = 0, \\ . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \\ \rho L + \frac{\partial T_{lx}}{\partial x} + \frac{\partial T_{ly}}{\partial y} + \frac{\partial T_{lz}}{\partial z} + \frac{\partial T_{ll}}{\partial l} = 0. \end{array}\right\} \; . \; . \quad (13)$$

Inserting (12) in the six equations of momenta (10), transforming again the surface integrals into volume integrals, and using (13), six conditions of equilibrium are derived:

$$T_{xy} = T_{yx}, \quad T_{xz} = T_{zx}, \quad . \; . \; . \; . \quad (14)$$

that is, the tensor T is symmetrical.

If we introduce the real axis of time and denote c the velocity of light propagation, we obtain for T the following expression:

$$T=\left|\begin{array}{cccc} T_{xx}, & T_{xy}, & T_{xz}, & \frac{iS_{xt}}{c} \\ T_{yx}, & T_{yy}, & T_{yz}, & \frac{iS_{yt}}{c} \\ T_{zx}, & T_{zy}, & T_{zz}, & \frac{iS_{zt}}{c} \\ \frac{iS_{tx}}{c}, & \frac{iS_{ty}}{c}, & \frac{iS_{tz}}{c}, & -W \end{array}\right| \; . \; . \; . \; . \quad (15)$$

We note that the expression for the forces, and the "law of energy" in electrodynamics are only particular cases of our equations of equilibrium.

§ 6. *The Equations of Motion.*

Following the classical mechanics, we take as equations of motion to a first approximation :

$$\left.\begin{aligned}
\mu\frac{d}{d\tau}\left(\frac{dx}{d\tau}\right) &= \rho\mathrm{F}_x+\frac{\partial\mathrm{T}_{xx}}{\partial x}+\frac{\partial\mathrm{T}_{xy}}{\partial y}+\frac{\partial\mathrm{T}_{xz}}{\partial z}+\frac{1}{c^2}\frac{\partial\mathrm{S}_{xt}}{\partial t},\\
\mu\frac{d}{d\tau}\;\frac{dy}{d\tau}\Big) &= \rho\mathrm{F}_y+\frac{\partial\mathrm{T}_{yx}}{\partial x}+\frac{\partial\mathrm{T}_{yy}}{\partial y}+\frac{\partial\mathrm{T}_{yz}}{\partial z}+\frac{1}{c^2}\frac{\partial\mathrm{S}_{yt}}{\partial t},\\
&\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\\
\mu c\frac{d}{d\tau}\left(\frac{dt}{d\tau}\right) &= \rho\mathrm{F}_t+\frac{\partial\mathrm{S}_{tx}}{c\partial x}+\frac{\partial\mathrm{S}_{ty}}{c\partial y}+\frac{\partial\mathrm{S}_{tz}}{c\partial z}+\frac{\partial\mathrm{W}}{c\partial t},
\end{aligned}\right\}. \quad (16)$$

where

$d\tau=\sqrt{1-\frac{v^2}{c^2}}dt$, μ is the density of "mass," and ρ of "charge."

From (16) follows that not only volume forces and gradient of surface forces influence motion, but also gradient (or absorption and emission) of momentum.

II. THE DYNAMICS OF ELECTROMAGNETIC FIELD.

§ 7. *The Laws of Equilibrium.*

Classical electrodynamics rests on double foundation : the electromagnetic field is wholly given by Maxwell's equations, so that every solution which satisfies them represents a possible state of field ; the dynamics of an electron is based upon the general dynamical principles of a material body (rigid or deformable) in connexion with Maxwell's field laws.

If we consider that the general principles of dynamics can be applied to the electromagnetic field, that the latter is only a particular instance of a mechanical system, then there must exist some general dynamical conditions, which are to be satisfied by the field as by other similar mechanical systems.

On the other hand, in conformity with Maxwell's point of view, laws of electricity are only laws of the electromagnetic field itself, hence the dynamics of the electron must be based not upon any assumption about the form, sizes, and other properties of the electron, but mainly from the dynamical laws of the electromagnetic field itself.

The considerations of the previous chapter suggest the application to the electromagnetic space, whether there exists a field or not, of the general conditions of equilibrium and motion of a continuous medium (13) (16).

According to electrodynamics the tensor T has the value:

$$\left.\begin{aligned} T_{xx}&=\frac{1}{8\pi}(X^2-Y^2-Z^2+\alpha^2-\beta^2-\gamma^2),\\ T_{xy}&=\frac{1}{4\pi}(XY+\alpha\beta),\\ S_{xt}&=\frac{c(Y_{\gamma}-Z_{\beta})}{4\pi},\\ W&=\frac{1}{8\pi}(X^2+Y^2+Z^2+\alpha^2+\beta^2+\gamma^2),\end{aligned}\right\} \quad \ldots \quad (17)$$

where X, Y, Z is the electric, and α, β, γ the magnetic forces.

§ 8. *Radiation.*

Let us find what form of solutions of Maxwell's equations is compatible with our general laws of equilibrium.

Let the solution be composed of terms $\frac{f}{r^n}$, where f is a function finite over the whole field; then T will consist of terms $\frac{f_1}{r^{2n}}$.

Now, if we integrate the equations of equilibrium over the whole field, we find that if $n \geqq 1$ the resultant stress will be finite, but the electromagnetic momentum and energy infinite unless n is equal to or more than $\frac{3}{2}$ both for the electric and magnetic field. But in this case the Poynting vector $\int \operatorname{div} S \, dv$ taken over the whole field vanishes, or there will be no radiation.

Hence we come to the conclusion that radiation by an electron in continuous motion is incompatible with the mechanical equilibrium of the electromagnetic field.

Radiation can go on only by discontinuous short pulses. These results agree with N. Bohr's model of the atom.

§ 9. *Motion.*

We apply the general laws of motion (16) to the field. Integrating over the volume of the electron and the electromagnetic space we find:

$$\left.\begin{aligned} m\frac{d}{d\tau}\frac{dx}{d\tau} &= \mathrm{F}_x - \int \operatorname{div} \mathrm{T}_x\, dv - \frac{1}{c^2}\int \frac{d\mathrm{S}_{tx}}{dt}\, dv, \\ m\frac{d}{d\tau}\frac{dy}{d\tau} &= \mathrm{F}_y - \int \operatorname{div} \mathrm{T}_y\, dv - \frac{1}{c^2}\int \frac{d\mathrm{S}_{ty}}{dt}\, dv, \\ &\cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ mc\frac{d}{d\tau}\frac{dt}{d\tau} &= \mathrm{F}_t - \frac{1}{c}\int \operatorname{div} \mathrm{S}_t\, dv - \frac{1}{c}\int \frac{d\mathrm{W}}{dt}\, dv. \end{aligned}\right\} \quad . \; . \; . \; (18)$$

where $d\tau = \sqrt{1 - \frac{q^2}{c^2}}\, dt$; and F_x, F_y. F_t is the external force

$$e\left(\mathrm{E} + \left[\frac{q}{c}\mathrm{H}\right]\right), \quad \frac{(q\mathrm{F})}{c};$$

the tensor T relates to the field of the electron, therefore we have taken the negative sign.

Now, as according to § 8 all div T vanish, we obtain from (18) the laws of motion of the electron in the electrodynamics.

§ 10. *The Law of Energy.*

It is accepted in the electrodynamics to look on the time projection of the conditions of equilibrium as the law of energy; but this is only an equation of motion of the same kind as the first three. On the other hand, the law of energy of a material point represents an invariant property of the four-dimensional space, therefore we must in this case look also for a similar law.

We multiply our equations (18) with dx, dy, dz, $-c\,dt$ respectively and add them:

$$(\mathrm{F}q) - \mathrm{F}_t c - \left(\frac{q}{c^2}\int \frac{d}{dt}\mathrm{S}_t\, dv\right) + \int \frac{d\mathrm{W}}{dt}\, dv = 0, \quad . \quad (19)$$

where F is the space part of the four-force, and q the velocity. As

$$\mathrm{F}_t c - \frac{d\mathrm{W}}{dt} = mc^2\frac{d}{dt}\frac{1}{\sqrt{1 - \frac{q^2}{c^2}}},$$

we obtain from (19)

$$(\mathrm{F}q)=\frac{d}{dt}\frac{mc^2}{\sqrt{1-\frac{q^2}{c^2}}}+\left(\frac{q}{c^2}\int\frac{d\mathrm{S}_t}{dt}dv\right), \quad . \quad . \quad (20)$$

or the work done by the external forces is spent on the increase of the kinetic energy of the electron and overcoming the electromagnetic resistance of the field.

If the motion is accompanied by heat generation, then, as we shall see later, the left side of (19) is equal not to zero but to $-\mathrm{R}$, when R is the heat absorbed by the electron.

Hence the generalized law of energy will be

$$(\mathrm{F}q)+\mathrm{R}=\frac{d}{dt}\frac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}}+\left(\frac{q}{c^2}\int\frac{d\mathrm{S}_t}{dt}dv\right), \quad . \quad (21)$$

or to the work of the external forces is added also the absorbed heat.

The expression (20) of the law of energy, where there is no heat generation, is an invariant of the four-dimensional space; the left side being zero in all systems of reference. But in case of radiation the law (21) will not be invariant; to have such law we must multiply the equations of motion (16) by $dx\,dy\,dz\,dt$, integrate over four-dimensional volume and take the change of energy for an element of track. It is easily seen that this invariant law of energy has the dimensions of action.

It may, perhaps, explain why Planck's universal constant of radiation has also the dimensions of action.

If we insert in (19) for the electric momentum and energy the values given by Theory of Relativity (see M. Laue, 'Die Relativitätstheorie,' p. 134, 1921), and remember that

$$(\mathrm{F}q)-\mathrm{F}_t c=0,$$

we obtain

$$\left(\frac{q}{c^2}\int\frac{d\mathrm{S}_t}{dt}dv\right)-\int\frac{d\mathrm{W}}{dt}dv=q\frac{d}{dt}\frac{4}{3}\frac{q}{c^2\sqrt{1-\frac{q^2}{c^2}}}\mathrm{E}^0$$

$$-\frac{d}{dt}\frac{c^2+\frac{1}{3}q^2}{c^2\sqrt{1-\frac{q^2}{c^2}}}\mathrm{E}^0=\frac{\frac{d}{dt}\sqrt{1-\frac{q^2}{c^2}}\mathrm{E}_0}{3} \quad (22)$$

(*ibid*. p. 226), or if q is not constant, the law of energy is not satisfied.

This contradiction arises because the Lorentz transformations and our law of motion for the electromagnetic field can be considered as valid for variable velocities only to the first approximation.

III. THE DYNAMICS OF A MATERIAL POINT.

§ 11. We apply the four-dimensional dynamics to one particular instance: to a material point moving with heat generation. In this case the fourth law of motion is not a sequel of the first three, the time projection of force can have an arbitrary value, and in order to describe the motion we must use all four equations.

§ 12. *The Law of Energy.*

We have seen that the force is normal to the track. If we denote the scalar product of the force and the track $(\mathrm{F}d\tau)$ as the four-dimensional work, we can say that in case of motion without heat effect the work

$$(\mathrm{F}d\tau)=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

But in the general case, where heat is absorbed or emitted,—the force is not normal to the track, and the work does not vanish; it is equal to

$$(\mathrm{F}d\tau)=\mathrm{X}\,dx+\mathrm{Y}\,dy+\mathrm{Z}\,dz-\mathrm{L}c\,dt=-d\mathrm{R}, \quad . \quad (24)$$

where the right side represents the heat absorbed by the moving body (if $d\mathrm{R}>0$).

This expression is the most general law of energy for a material point.

In so far as the analytical expression (24) is concerned, it can be applied not only to an electron but to a finite piece of matter, but the physical phenomenon is different in these cases.

1. We consider an electron. We have from (24)

$$\mathrm{X}\,dx+\mathrm{Y}\,dy+\mathrm{Z}\,dz+d\mathrm{R}=\mathrm{L}c\,dt, \quad . \quad . \quad . \quad (25)$$

which expresses that the work of the external forces and the absorbed heat is equal to the increase of the time (or kinetic) energy.

Now the energy of an electron (or proton), as its charge is constant, can be increased only if its velocity increases; hence the absorption (emission) of heat is accompanied by increase (decrease) of its velocity.

2. Quite different appears this phenomenon in a material body. Its time energy consists of the energy of its motion as a whole, and the energy of the electrons and protons.

Absorption by a material body goes on through its electrons and protons, it increases their energy (or the temperature of the body) but leaves unchanged the velocity of the body as a whole.

These considerations have a bearing on the kinetic theory of matter.

§ 13. *Impulsive Forces.*

Now there arises the question: How can a motion be physically realized, where the force is inclined to the track?

A straight answer gives us the geometry of motion. If the track is discontinuous, the radius of curvature has two directions, and, hence, is not normal to the track at the singular point.

This case corresponds to impulsive forces in dynamics.

§ 14. *Elastic Forces.*

Let us have a material body at rest. We apply to it some impulsive force, and it acquires a velocity v. If $X\Delta t$ is the impulse, then $mv = X\Delta t$. The acquired kinetic energy is $\frac{mv^2}{2}$, the work done by the impulsive force is

$$X\Delta t \cdot \frac{v}{2} = \frac{mv^2}{2},$$

or equal to the acquired kinetic energy. The whole impulse is spent on increase of velocity.

We consider now this problem from the point of view of the four-dimensional dynamics.

The equations of motion are:

$$\left.\begin{aligned} m\frac{d}{d\tau}\frac{dx}{d\tau} &= X, \\ m\frac{d}{d\tau}\frac{dl}{d\tau} &= L, \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (26)$$

where $d\tau^2 = dx^2 + dl^2$.

To integrate (26) we denote:

$$\frac{dx}{d\tau} = \sin\phi, \quad \frac{dl}{d\tau} = \cos\phi, \quad \ldots\ldots \quad (27)$$

and as $\frac{d}{d\tau} = \cos\phi\frac{d}{dl}$, (26) become

$$\left.\begin{aligned} m\frac{d}{dl}\left(\frac{\cos\phi\sin\phi + \phi}{2}\right) &= X, \\ \frac{m}{2}\frac{d}{dl}\cos^2\phi &= L, \end{aligned}\right\} \quad \ldots\ldots \quad (28)$$

or introducing the real time, and denoting c the velocity of light, we obtain

$$\left.\begin{aligned} -icm\frac{d}{dt}\left(\frac{\cos\phi\sin\phi+\phi}{2}\right)&=\mathrm{X}, \\ \frac{mc}{2}\frac{d}{dt}\cos^2\phi&=\mathrm{L}, \end{aligned}\right\} \quad . \ . \ . \ (29)$$

where

$$\sin\phi=\frac{\frac{iv}{c}}{\sqrt{1-\frac{v^2}{c^2}}}; \quad \cos\phi=\frac{1}{\sqrt{1-\frac{v^2}{c^2}}}.$$

Applying (29) to our case, we have

$$\left.\begin{aligned} -icm\left[\frac{\cos\phi\sin\phi+\phi}{2}\right]_0^v&=\mathrm{X}\Delta t, \\ \frac{mc}{2}\left[\cos^2\phi-1\right]_0^v&=\mathrm{L}\Delta t. \end{aligned}\right\} \quad . \ . \ (30)$$

We write the equation of energy. For this purpose we multiply the first of (30), as $v=-ic\cos\phi\sin\phi$, with

$$v_1=-ic\sin\frac{\phi}{2}\cos\frac{\phi}{2},$$

the second with $-c$, and add them :

$$\mathrm{R}=\mathrm{X}v_1\Delta t-\mathrm{L}c\Delta t=-mc^2\left(\frac{\cos\phi\sin\phi+\phi}{2}\right)\frac{\sin\phi}{2}$$
$$-\frac{mc^2}{2}(\cos^2\phi-1), \quad . \ . \ . \ (31)$$

and it is easily seen that this expression will not be equal to zero.

For small velocities

$$\mathrm{R}=\frac{mv^4}{12c^2}, \quad . \ . \ . \ . \ . \ . \ . \ (32)$$

or the work is greater than the increase of the kinetic energy ; the difference R is lost by radiation.

If we consider a more general case, where the initial velocity v_1 is changed by impulsive force into v_2, we find that the heat effect is

$$\frac{m}{12c^2}(v_2+v_1)^3(v_2-v_1), \quad . \ . \ . \ . \ . \ (33)$$

or if $v_2>v_1$ there is radiation of $v_2<v_1$—absorption.

§ 15. *Elastic Collisions.*

Let us have two material points moving with velocities v_1 and v_2 respectively. They collide. What effect will be produced?

From (29) we have

$$\left.\begin{aligned} &-icm_1\frac{d}{dt}\left(\frac{\cos\phi_1\sin\phi_1+\phi_1}{2}\right)\\ &\quad-icm_2\frac{d}{dt}\left(\frac{\cos\phi_2\sin\phi_2+\phi_2}{2}\right)=X_1+X_2=0,\\ &\frac{m_1c}{2}\frac{d}{dt}\cos^2\phi_1+\frac{m_2c}{2}\frac{d}{dt}\cos^2\phi_2=L_1+L_2=0. \end{aligned}\right\} \quad . \quad (34)$$

Hence if ϕ_1' and ϕ_2' are the corresponding angles after collision we have from (34)

$$\left.\begin{aligned} &m_1\cos\phi_1\sin\phi_1+m_1\phi_1+m_2\cos\phi_2\sin\phi_2+m_2\phi_2\\ &=m_1\cos\phi_1'\sin\phi_1'+m_1\phi_1'+m_2\cos\phi_2'\sin\phi_2'+m_2\phi_2',\\ &m_1\cos^2\phi_1+m_2\cos^2\phi_2=m_1\cos^2\phi_1'+m_2\cos^2\phi_2', \end{aligned}\right\} \quad (35)$$

two transcendental equations, which define the motion after collision.

For small velocities (35) becomes the well-known conditions of elastic collision in classical mechanics.

The energy lost or gained by radiation during the collision is from (33), (35),

$$\frac{4}{3}\frac{m_1m_2}{c^2}\frac{(m_1v_1+m_2v_2)^3}{(m_1+m_2)^4}(v_2-v_1), \quad . \quad . \quad . \quad (36)$$

or the heat effect is equal and opposite in the two material points.

§ 16. *Heat.*

This analysis elucidates some of the laws of matter.

1. Heat is not a result of continuous motion of molecules. A material point in continuous motion does not generate heat, and there is no reason why a great number of them should produce this effect. Heat generation arises solely from discontinuous motion.

At the absolute zero only continuous motion is possible.

2. If electrons and protons (a gas) are enclosed in a vessel, so that no heat interchange is possible with the outer space, once brought in motion, they will indefinitely continue it.

This does not apply to finite pieces of matter, which, as we have seen (§ 12), would soon stop.

XCI. *The X-Ray Spectra of the Lower Elements.*

By ROBERT THORÆUS [*].

[Plates XVII. & XVIII.]

PART II.

IN connexion with the recently published wave-length measurements within the K- and L-series of the lower elements [†] some observations have been made concerning the structure and general appearance of these X-ray spectra. Some new wave-lengths have also been measured.

When studying the earlier wave-length tables of the lower L-series it was found that the main lines α and β_1 are accompanied by only one satellite called α_3. By using the new high-vacuum spectrograph with a gypsum crystal that gives a rather good dispersion within this range of wave-lengths, both the main lines have been proved to be more complicated. As far as can now be stated, they have two satellites each that have been measured for the elements Br (35) to Cu (29). Prof. M. Siegbahn has proposed to denote these four satellites α', α'', β', and β''. When doing this it must, however, be pointed out that the line called α', as far as can be stated from the wave-lengths, may be the same one as the earlier α_3 line. The intensity of the satellites on the plates is rather good. When passing from Zn (30) to Cu (29) a very interesting case appears. The satellites of Zn are rather well-defined and relatively strong, but in the case of Cu and still more that of Ni (28) they are very diffuse and tend to disappear in the continuous blackening on the photographic plate. Owing to this, it has not been possible to measure them for elements below Ni (28).

The L-series of Ge (32) lie just within the range of elements investigated here, but they have never before been completely measured, as this element and its compounds are very rare. By friendly help, however, from Dr. L. M. Dennis of Cornell University, U.S.A., I was able to get a small amount of metallic germanium quite sufficient for my exposures. The powdered metal was applied on a scratched aluminium plate dovetailed in the copper anticathode.

In some cases I have also been able to measure the very faint emission lines $\beta_3\,\beta_4$. It was not, however, possible to separate them, and so I have given only a mean value.

---

[*] Communicated by Prof. Manne Siegbahn, D.Sc.

[†] Phil. Mag. February 1926.

In order to extend the knowledge of the K- and L-series, I have also made some attempts to photograph the K-series of oxygen and the L-series of vanadium with palmitic acid as crystal. In the case of oxygen fine-powdered quartz SiO_2, was applied on the scratched copper anticathode. After an exposure of about two hours with 35 milliamps and 5000 volts, I found three lines on the photographic plate. For identifying the lines, I had arranged, just before the plate, a cross-wire that left a white shadow on the plate. As the position of this shadow was known, I had no difficulty in identifying one of the lines as SiKα in the third order, and taking this line as reference the other lines could easily be measured. In the following Table I. I give the calculations.

For taking the L-series of vanadium I have used ferro-vanadium as anticathode substance. This alloy contained about 45 per cent. Va, and was kindly supplied by the Metallographic Institute in Stockholm. The method of identifying the lines was the same as mentioned above. The calculations are to be found in Table II.

In Part I. I gave the wave-lengths of the strongest lines of the lower L-series. In Table III. I have now collected these values together with the new ones, and Tables IV. and V. give the calculated ν/R and $\sqrt{\nu/R}$ values. Complementary to this, I have also drawn the diagram in fig. 1, containing all the up to date known wave-lengths of the lower L-series. Here the Lα lines are arranged on a vertical, and the other ones are set up from the scale given in the diagram. It is clearly to be seen how the displacement of

Fig. 1.

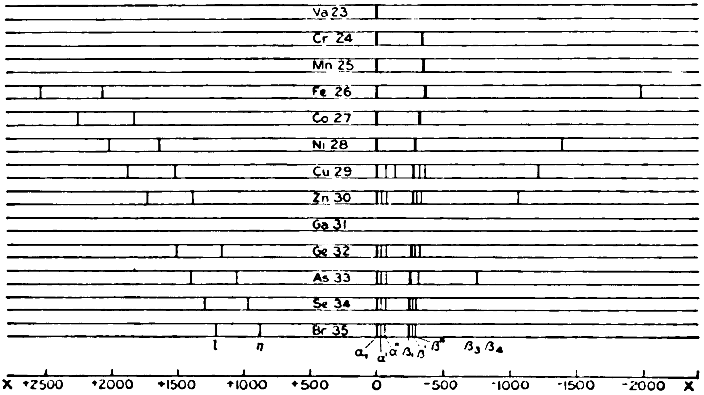


TABLE I.

Plate No.	Line No.	Intensity.	Distance, mm.	Correction, $\Delta\phi$.	ϕ.	λ.	ν/R.	$\sqrt{\nu/R}$.	
T. 246	1	...	Ref.	—	17° 29′	21·33	...	...	Si $K\alpha_{III}$.
	2	...	+ 9·3	+2° 3′	19° 32′	23·73	38·40	6·197	O $K\alpha$.
	3	...	+20·5	+4° 38′	22° 1′	26·61	...	...	Cu $L\alpha_{II}$.

TABLE II.

Plate No.	Line No.	Intensity.	Distance, mm.	Correction, $\Delta\phi$.	ϕ.	λ.	ν/R.	$\sqrt{\nu/R}$.	
T. 247	Cross-wire.	...	Ref.	—	20° 12′				
	1	...	−1·7	−0° 16′	19° 56′	24·2	37·7	6·13	Va $L\alpha$.

TABLE III.

Wave-length Values of the lower L-Series.

Wave-lengths in Å.U.

	Br 35.	Se 34.	As 33.	Ge 32.	Zn 30.	Cu 29.	Ni 28.	Co 27.	Fe 26.	Mn 25.	Cr 24.	Va 23.
l	9·563	10·271	11·047	11·920	13·95	15·19	16·55	18·20	20·12			
η	9·234	9·939	10·710	11·585	13·61	14·83	16·17	17·77	19·65			
$\alpha_{1,2}$	8·357	8·971	9·650	10·414	12·224	13·308	14·528	15·94	17·58	19·39	21·53	24·2
α'	8·326	8·939	9·616	10·378	12·191	13·24						
α''	8·297	8·903	9·581	10·341	12·150	13·172						
β_1	8·103	8·717	9·394	10·152	11·958	13·029	14·235	15·62	17·22	19·04	21·19	
β'	8·086	8·698	9·372	10·131	11·934	12·99						
β''	8·065	8·671	9·346	10·102	11·893	12·93						
β_4 β_3	...	...	8·911	...	11·16	12·10	13·14	...	15·61			

some groups of lines increases very much, especially that of the $l\eta$ and $\beta_3\beta_4$ lines. In the case of Fe (26) the distance between the $l\eta$- and the $\alpha_1\beta_1$-groups is about 2·5 Å.U., that is more than six times the distance between the lines within each group.

Concerning the $L\alpha$ line something peculiar seems to happen in the range of Zn and Cu. In the case of Zn this line is rather sharp, slightly broader than the slit, but the $L\alpha$ of Cu and still more that of Ni is very broad and diffuse. As this also appears when using a mica crystal, it cannot be simply connected with the increased dispersion, and so I have performed a special investigation concerning the $L\alpha$ lines of Zn, Cu, and Ni in different chemical states. The $L\alpha$ lines have been examined for the following substances :—

1. *Zinc* : Zn (met.), ZnO, and ZnS.
2. *Copper* : Cu (met.), Cu_2O, CuO, and CuS.
3. *Nickel* : Ni (met.), NiS, and Ni_2O_3.

All the compounds were applied on aluminium plates, as mentioned above. The results are rather surprising. In the case of Zn the $L\alpha$ lines are all alike, but for Cu and Ni their general appearance changes very thoroughly. The $L\alpha$ of Cu (met.) and Cu_2O are quite alike, a very broad line with diffuse edges, but for CuO and CuS they consist of *two lines clearly separated* and each of them of about the same breadth as the $L\alpha$ of Zn. Thus the metallic and monovalent Cu behave in the same way, but the bivalent Cu quite differently. In the case of Ni I have found that the metallic and bivalent ones are equal, but the trivalent atom in Ni_2O_3 seems to give a separated $L\alpha$ line, although not so sharply defined. In fig. 2 (Pl. XVII.) I supply the photometer curves of Cu $L\alpha$ from CuO, where the separated lines are clearly to be seen. The curves are taken on three different places of the photographic plate. In fig. 3 (Pl. XVIII.) some photograms of different L-series are collected. All of them are taken with a gypsum crystal.

In Part I. I gave a diagram showing how the wave-length difference $L\alpha - L\beta_1$ runs very smooth down to Zn (30), but for Cu (29) and the following elements belonging to the iron group behaves quite differently. Now the observations concerning the structure and general appearance of the $L\alpha$ line seem to point in the same direction. Down to Zn the structure and intensity of both the $L\alpha$ and the $L\beta_1$ lines are quite regular, but at copper they have suddenly changed very considerably. The $L\alpha$ line is very broad and diffuse, and in

TABLE IV.

ν/R Values of the lower L-Series.

	Br 35.	Se 34.	As 33.	Ge 32.	Zn 30.	Cu 29.	Ni 28.	Co 27.	Fe 26.	Mn 25.	Cr 24.	Va 23.
l	95·3	88·7	82·5	76·5	65·3	60·0	55·1	50·1	45·3			
η	98·7	91·7	85·1	78·7	67·0	61·5	56·4	51·3	46·4			
$\alpha_{1,2}$	109·1	101·6	94·4	87·5	74·55	68·5	62·7	57·2	51·8	47·0	42·3	37·7
α'	109·5	101·9	94·8	87·8	74·8	68·8						
α''	109·8	102·4	95·1	88·1	75·0	69·2						
β_1	112·4	104·5	97·0	89·8	76·2	69·94	64·0	58·3	52 9	48·0	43·0	
β'	112·7	104·8	97·2	90·0	76·4	70·2						
β''	113·0	105·1	97·5	90·2	76·6	70·3						
$\left.\begin{matrix}\beta_4\\ \beta_3\end{matrix}\right\}$	...	...	102·3	...	81·7	75·3	69·36	...	58·4			

TABLE V.

$\sqrt{\nu/R}$ Values of the lower L-Series.

	Br 35.	Se 34.	As 33.	Ge 32.	Zn 30.	Cu 29.	Ni 28.	Co 27.	Fe 26.	Mn 25.	Cr 24.	Va 23.
l	9·762	9·419	9·083	8·746	8·082	7·746	7·421	7·076	6·730			
η	9·934	9·576	9·224	8·87	8·183	7·839	7·507	7·161	6·810			
$\alpha_{1,2}$	10·442	10·079	9·718	9·354	8·634	8·275	7·920	7·561	7·200	6·855	6·506	6·13
α'	10·47	10·09	9·74	9·37	8·65	8·295						
α''	10·48	10·12	9·75	9·386	8·66	8·32						
β_1	10·602	10·225	9·850	9·476	8·730	8·365	8·001	7·637	7·275	6·923	6·558	
β'	10·62	10·24	9·86	9·487	8·74	8·38						
β''	10·63	10·25	9·874	9·497	8·752	8·385						
$\left.\begin{matrix}\beta_4\\ \beta_3\end{matrix}\right\}$	...	...	10·12	...	9·04	8·68	8·33	—	7·64			

the case of Ni it is most diffuse against longer wave-lengths. The intensity of the $L\beta_1$ is smaller when compared with that of the $L\alpha$, all the satellites are very faint and, moreover, from the diagram fig. 1 it will be seen how they are somewhat displaced. So there are many facts that appear simultaneously in the same range of elements, but it is difficult to say whether they are of the same character or not.

The irregularity of the wave-length difference may refer to some disturbances in the energy levels L_{II} L_{III} probably connected with the magnetic properties of the iron group elements. This suggestion seems to be supported by the observation that the deviation is biggest in the case of iron, and that a similar effect also appears within the K-series of these elements. Now we may also imagine that the above-mentioned sudden change of the structure and intensity within the L-spectra refers to some magnetic disturbances. Further, it may be due, more or less, to some changes of the electronic arrangement in the energy levels M_{IV} M_V that is connected with the electronic building-up process by which, in the range of these elements, the energy levels just mentioned probably get their electronic equipment.

In the case of bivalent Cu the $L\alpha$ line was found to consist of two lines. This may be due to the chemical state of the Cu atom. In recent papers Mr. E. Bäcklin * and Mr. B. B. Ray † have found such changes in the $K\alpha$ line of S (16) when using different compounds. As the $K\alpha_1$ and $K\alpha_2$ lines were quite separated, they got three lines on the photographic plate. In my case the $L\alpha_1$ and $L\alpha_2$ lines are not separated, and so, if due to the same effect, only two lines might be expected.

From the ν/R values of the new wave-lengths some energy-levels can also be determined. The following transitions are then to be considered :—

$$M_I = \begin{cases} L_{II} - L\eta \\ L_{III} - Ll \end{cases}$$

$$M_{II,III} = K_I - K\beta_1$$

$$M_{IV} = L_{II} - L\beta_1$$

$$M_{IV,V} = L_{III} - L\alpha_1.$$

The K- and L-absorption edges of the elements in question are, however, not very accurately measured. Mr. E. Åse, in

---

* *Zeits. f. Physik*, Bd. xxxiii. Heft 7 (1925).

† Phil. Mag. Sept. 1925.

TABLE VI.

ν/R Values of the Energy Levels

Element No.	K_I.	L_{II}. $K_I-K\alpha_2$.	L_{III}. $K_I-K\alpha_1$.	M_I.		$M_{II, III}$. $K_I-K\beta_1$.	M_{IV}.	$M_{IV, V}$.
				$L_{II}-L\eta$.	$L_{III}-Ll$.			
35 Br	992·57	117·69	114·29	18·99	18·99	13·50	5·29	5·19
34 Se	932·02	108·37	105·40	16·67	16·70	11·57	3·87	3·80
33 As	874·01	100·02	97·42	14·92	14·92	10·36	3·02	3·02
30 Zn	711·73[1]	77·10	75·39	10·10	10·09	6·80	0·90	0·84
29 Cu	661·59[1]	70·32	68·84	8·82	8·84	5·68	0·38	0·36
28 Ni	614.12[1]	64·70	63·37	8·30	8·27	5·40	0·70	0·67
27 Co	568·24[1]	59·04	57·80	7·74	7·70	4·73	0·74	0·60
26 Fe	524·00[1]	53·44	52·40	7·04	7·10	4·17	0·54	0·60
25 Mn...............	481·83[1]	48·18	47·34	—	—	3·70	0·18	0·34
24 Cr	441·23[1]	43·12	42·40	—	—	3·61	0·12	0·10

[1] These values are kindly supplied by Mr. E. Ase, and belong to the metallic form of the elements.

this laboratory, has recently been working with measurements in this region, and from his not yet published results he has kindly supplied me those of his new values which are necessary for the above calculations—that is, the K-absorption edges of the elements Zn (30)–Cr (24). Because of waiting for these values the publication of this paper has been somewhat delayed in order to get the content as complete as possible.

From the K-levels as measured by Åse I have calculated the values of the L_{II}, L_{III}, and $M_{II,III}$ levels by using Siegbahn and Dolejšek's precision-measurements within the K-series of these elements *. By the above formulas the M_{I}, M_{IV}, and $M_{IV,V}$ levels are then calculated. In Table VI. I have collected all the energy-levels.

By combining the doublet $Ll\eta$ and the levels L_{II} and L_{III} I have obtained two values of the M_{I} level. As can be seen from the table the agreement is very good. The difference between two corresponding values never amounts to 1 per cent.

The following Table VII. gives the $\sqrt{\nu/R}$ values of the energy-levels as calculated from Table VI.

In the diagram fig. 4 the $\sqrt{\nu/R}$ values of the M-levels are plotted against the atomic number Z. From this diagram it is clearly to be seen how a sudden change in the slope of the curves just appears at Cu (29), thus corresponding to the above-mentioned changes observed in the structure and general appearance of the L-series of these elements.

Somewhat aside from the subject dealt with above, I supply the drawings (Pl. XVII. fig. 5) of a small high-vacuum spectrograph that has proved to be rather convenient for finding the first approximate wave-length value of an unknown X-ray line. For this purpose there are no requirements of accuracy, and so the construction may be kept quite simple. The photograms are taken on circular bent film-strips 162 × 23 mm. in size and placed at a distance of 85 mm. from the reflecting surface of the crystal. As may be seen from the drawing, a cone is arranged for inserting the film-strip, the position of which is then quite fixed. This arrangement, however, only allows reflecting angles from 0 to about 40°. When this spectrograph is used a rather small dispersion is wanted, that means in general small angles, and the satisfying of this condition raises no difficulties. By choosing a crystal with large lattice-constant a reflecting angle smaller than the above maximum of 40° will easily be obtained. When an unknown X-ray line is to be approximately determined it is

---

* *Zeits. f. Physik*, Bd. x. Heft 3 (1922).

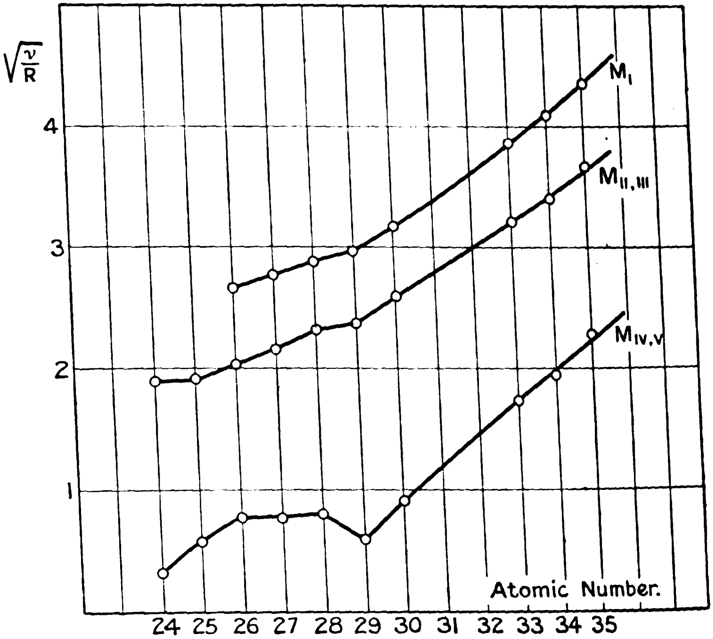
Table VII.

$\sqrt{\nu/R}$ Values of the Energy Levels.

Element No.	K_I.	L_{II}.	L_{III}.	M_I.		$M_{II,III}$.	M_{IV}.	$M_{IV,V}$.
				$L_{II}-L\eta$.	$L_{III}-Ll$.			
35 Br	31·51	10·85	10·69	4·36	4·36	3·67	2·30	2·28
34 Se	30·53	10·41	10·27	4·08	4·09	3·40	1·97	1·95
33 As	29·56	10·01	9·87	3·86	3·86	3·21	1·74	1·74
30 Zn	26·68	8·78	8·68	3·18	3·17	2·61	0·95	0·92
29 Cu	25·72	8·39	8·30	2·97	2·97	2·38	0·62	0·60
28 Ni	24·78	8·04	7·96	2·88	2·88	2·32	0·84	0·82
27 Co	23·84	7·68	7·60	2·78	2·77	2·17	0·86	0·77
26 Fe	22·89	7·31	7·24	2·65	2·66	2·04	0·73	0·77
25 Mn...............	21·95	6·94	6·88	—	—	1·92	0·42	0·58
24 Cr	21·01	6·57	6·51	—	—	1·90	0·35	0·32

necessary to expose continuously over a rather big range of angle-values, and to run such an exposure within a suitable time requires a good intensity of the X-ray beam. To satisfy this requirement the slit is placed as near the anticathode as possible. The slit itself should be at least 0·2 mm. wide.

Fig. 4.



The crystal table is also of a very simple construction that, I think, will easily be seen from the drawing. The body of the spectrograph is built of 5 mm. brass plate and all soldered together. At the circumference of the upper plate is arranged a scale for reading the movement of the crystal. The spectrograph is then connected to the X-ray tube by a cone; this is quite necessary, to get a good tightening on this point. Other details, I think, will easily be understood when looking at the drawing.

In conclusion I wish to express my best thanks to Professor Manne Siegbahn, who has suggested me this work, for his kind interest and much valuable advice on different points during the whole investigation.

Upsala,
Physical Laboratory of the University,
April, 1926.

XCII. *Photophoresis of Colloidal Particles in Aqueous Solutions.* *By* WILFRED W. BARKAS, *M.Sc.* *

[Plate XIX.]

SUMMARY.

THE action of light and X-rays on aqueous solutions of copper, gold, silver, and gamboge is observed. The cloud of particles, settling out of suspension under the action of gravity, moves on the average towards the light side of the containing cell, being thus light negative on Ehrenhaft's convention. The upper surface of the cloud takes up a characteristic formation under the action of light, the boundary becoming much more sharply defined. The velocities of drift are calculated for particles near the top of the cloud; these are greater in most cases than the velocities found by Ehrenhaft for particles suspended in gases and illuminated by the intense beam of the ultra-microscope. The change of size of gold particles under the action of light is also measured.

WHILE determining the sizes of colloidal copper particles in aqueous solutions, by the method of observing the rate of fall of the cloud-surface, it was noticed that light had a strong action on the formation of the settling cloud. If the particles settled in the dark, the cloud surface was horizontal and the exact upper boundary indefinite over a vertical distance of about 0·5 mm. The radius given by this method, by Stokes's law, was, for the smallest particles which settled out, in good agreement with that determined by other methods, *e. g.* centrifuging or by the final variation of concentration with depth (Trans. Far. Soc. xxi., i. 1925). If, however, the solution was exposed to light, the cloud moved on the average towards the source of light, and its upper surface became more sharply defined than before.

A few preliminary experiments were made which are recorded here, the quantitative measurements being taken from a single set of observations, but qualitatively the results are quite general.

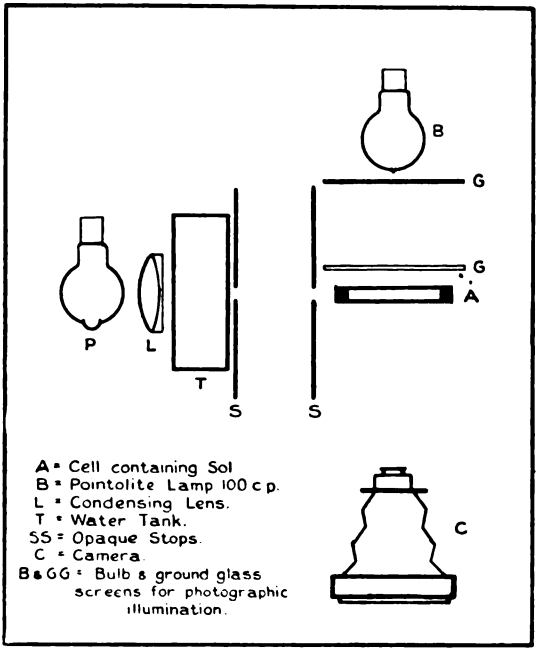
A glass-sided cell A (fig. 1), 7·7 cm. square and 1 cm. thick, was set up vertically containing a suspension of copper particles. The narrow face of the cell was illuminated by light from a 100-c.p. pointolite, P, placed at about 20 cm.

---

* Communicated by Prof. A. W. Porter, D.Sc., F.R.S.

away, the heat rays being absorbed by a large glass tank, T, 8 cm. thick. Except for the side facing the light, the cell was completely screened from all light rays by the opaque screens S, S. The broad face of the cell could be photographed in the camera, C, by means of transmitted light from a lamp, B, on the axis of the camera lens, diffused through two ground-glass screens G, G, an exposure of 30 seconds being required. This light was, of course, only used during the taking of photographs.

Fig. 1.

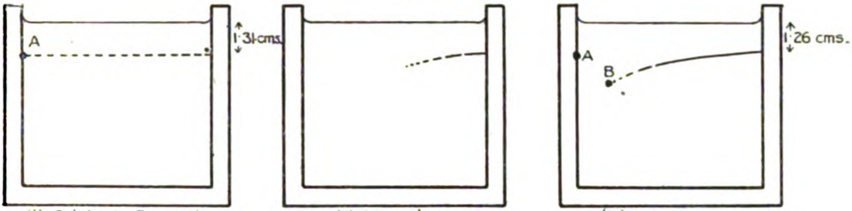


Plan of apparatus for photographing photophoresis of colloidal solutions.

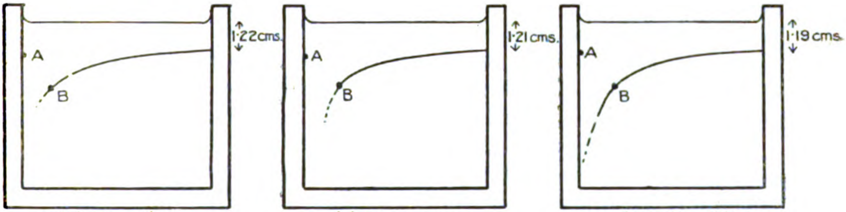
The photographs taken are mostly not good enough for half-tone production, though Plate XIX. gives representative prints corresponding to diagrams in fig. 2, nos. i., iii., and vi. The figures are drawn from the photographs. The curved line represents the upper surface of the cloud ; it is shown continuous where the cloud-surface is definite, and dotted where it is diffuse. The details of the experiment are as follows :—

After settling under gravity in the dark for 18 hours, two parallel diffuse cloud-surfaces can be seen (Pl. XIX., 1) at depths of 1·0 and 1·31 cm., indicating two predominant sizes of particles (3·15 and $3{\cdot}58 \times 10^{-6}$ cm. radius). When the activating light was turned on, on the right-hand side, both cloud-surfaces moved similarly to one another. Photographs were taken every half hour. Fig. 2, nos. i. to vi., show the change of formation of the lower of the two clouds only, up to $3\frac{1}{2}$ hours in the light ; after this, further change was very slow. The surface of this cloud became sharply defined on the right and disappeared completely on the extreme left (fig. 2, ii.). It gradually took up the new form, and finally became sharp over its entire length from the top right-hand to the bottom left-hand corner of the cell, the definition being now much sharper than in the original cloud (fig. 2, vi.). It should be noticed that the cloud-surface on the top right-hand side (*i. e.* the edge near the light) rises against gravity a distance of 0·05 cm., *i. e.* at a rate of $1{\cdot}4 \times 10^{-5}$ cm./sec. for the first hour, which is about 0·7 times the rate of fall under gravity in the dark.

Fig. 2.



(i) Original Formation. (Settling in dark). (ii) After ½ hour (iii) After 1 hour



(iv) After 1½ hrs. (v) After 2 hrs. (vi) After 3½ hrs.

Light on right-hand side (see Pl. XIX.). (The curved line represents the upper surface of the cloud ; a full line representing a sharp, and a dotted line a diffuse boundary.)

The movement of the cloud-surface indicates that the whole cloud is drawn over to the light side of the cell until equilibrium is set up; this equilibrium presumably being reached when the forces due to the light balance the osmotic pressure of the solution. If this is the case, we may obtain some idea of the speed of drift of the particles by considering, for example, a particle originally situated in the top left-hand corner of the cell in fig. 2 (at the point A in no. i.). If we make no assumption as to the direction of drift, it must move *at least* as far as to the nearest point on the cloud-surface (to the point B in nos. iii. to vi.). From the times taken this involves a minimum velocity of 5×10^{-4} cm./sec. for the first hour, or $1{\cdot}6 \times 10^{-4}$ cm./sec. for the whole period of 3½ hours. In the first hour this is 25 times the rate of fall under gravity in the dark. If we assume only horizontal drift (*i. e.* along the beam of light), the velocity of such a particle cannot be so definitely calculated, but it will be of the same order. For points lower down in the suspension the motion is in both cases smaller, though not in general zero.

This same suspension is afterwards left undisturbed in the dark for 17 hours. The top of the cloud is now roughly horizontal again, but very diffuse except for the edge previously nearest the light, which is still as sharp as before, but which in the case shown in the diagram has fallen to 1·35 cm. below the liquid surface, this velocity being $2{\cdot}6 \times 10^{-6}$ cm./sec., or only 0·13 that of the previous night.

After the cloud had been built up on the right as previously described, fig. 3 shows the effect of changing the light over to the left-hand side of the cell. A complete reversal of the cloud formation takes place in 40 minutes. For a particle originally at the point A (fig. 3, i.) this involves a least possible velocity of $1{\cdot}25 \times 10^{-3}$ cm./sec.

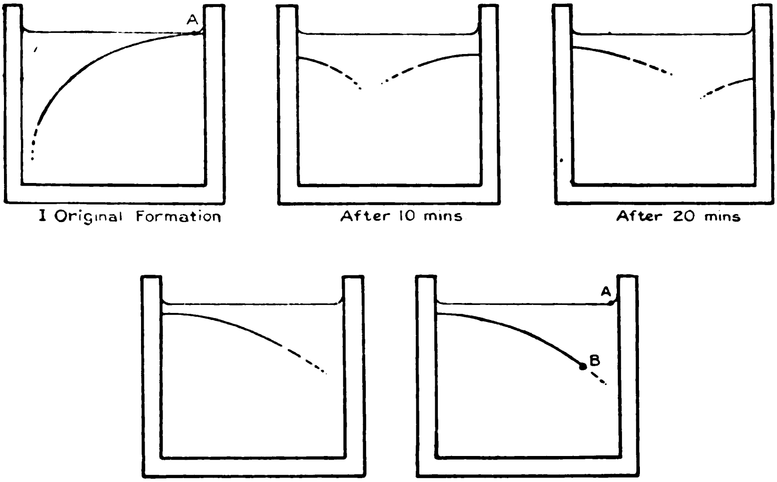
These velocities for the particular suspension under consideration may be summarized as follows:—

Fall of cloud under gravity		$2{\cdot}02 \times 10^{-5}$ cm./sec.
Particles at point A (fig. 2) on exposure to light	for 1st hour	$5{\cdot}0 \times 10^{-4}$ cm./sec.
	average of 3½ hours	$1{\cdot}64 \times 10^{-4}$ cm./sec.
Particles at A (fig. 3) on reversing direction of light	average for 3½ hours	$1{\cdot}25 \times 10^{-3}$ cm./sec.

In later experiments the beam of light was rendered parallel by the introduction of the lens L (fig. 1), but this made no apparent difference to the cloud formation.

If the suspension is illuminated as soon as it is set up, without giving time for the particles to settle down in the liquid, the reduction of volume of the cloud under the action of light is not measurably different from what it would have been if the cloud had settled for the same time under the action of gravity alone. Again, in the case of solution which had been left to stand for several weeks until it contained in suspension only those particles which remained permanently suspended by brownian movement (*i. e.* in which there was

Fig. 3.



I Original Formation

After 10 mins

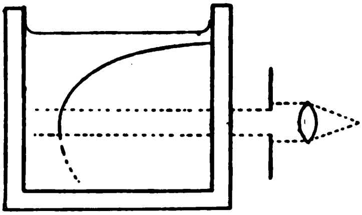
After 20 mins

After 30 mins.

After 40 mins.

Change of cloud-formation on changing light from right- to left-hand side.

Fig. 4.



Cloud formation due to a narrow parellel beam of light

no surface to the cloud of particles within the body of the solution), no cloud-surface was formed upon exposure to light. That this suspension was still rich in particles was confirmed by observation under the microscope. In the case illustrated in fig. 2, however, where settling had previously taken place, the volume of the cloud after

$3\frac{1}{2}$ hours was about 10 per cent. smaller than it would have been, in the same time, if acted on by gravity alone.

The next trial was made by illuminating the side of the cell by an accurately parallel beam of light from an arc lamp along the narrow parallel path shown by the dotted lines in fig. 4. In this case the cloud is drawn in at the bottom as well as at the top, the greatest horizontal width being in the beam of light. The cloud again becomes sharply defined, first at the top right-hand corner of the cell, though this is now well outside the direct illumination of the beam of light, and again this portion rises slightly against gravity.

These experiments were repeated with colloidal suspensions of gold, silver, and gamboge, the effects being in each case the same.

X-Rays.

A suspension of gold was exposed to a narrow penetrating beam of X-rays from a tungsten anti-cathode. In this case also the cloud drifted towards the source of X-rays, the formation being similar to that shown in fig. 4. It is not possible to compare the intensities of the X-rays and light used, but the time taken to build up the cloud was roughly the same in each case.

It cannot be assumed that the observed changes in cloud formation are due entirely to the action of light without other disturbances, such as temperature changes in the solution or slight convection currents to which the cloud would be very sensitive; and for this reason no attempt is here made to deduce a mathematical expression for the shape of the cloud-surface. It seems, however, that the light exerts a force on the particles, causing them to move towards the source of light, the greatest movements taking place nearest the top of the cloud where the concentration is least, in accordance with the laws of distribution of colloidal particles.

Change of Size of Gold Particles.

It was noticed that the colour of the gold suspension changed from ruby-red to deep mauve as a result of exposure to light, but that no such colour-change took place after exposure to X-rays. In one instance the change of colour along the narrow beam of light (as in fig. 4) could be seen quite distinctly, and remained visible for about an hour after the light had been turned off. The suspension previously exposed to X-rays changed colour on subsequent exposure to ordinary light.

Three samples of gold solution were taken from the same stock, one having been exposed to light, one to X-rays, and one having been kept in the dark. These were set up in hard glass test-tubes and allowed to settle in the dark for twelve days. The transition of colour from clear liquid at the top of the tube to dense solution below was indefinite over a depth of about 6 mm., showing that particles of all sizes were present (even after exposure to light); but the mean position of the cloud-surface was taken from the sixth to the twelfth day. This gave the mean size of gold particles in the solution as follows: —

	Radius.	Velocity.
Particles kept in the dark	$2{\cdot}3\times10^{-6}$ cm.	0·176 cm./day.
Particles exposed to X-rays	$2{\cdot}3\times10^{-6}$ „	0·176 „
Particles exposed to light	$2{\cdot}9\times10^{-6}$ „	0·272 „

These show a decided increase in size after exposure to light.

Ehrenhaft (*Ann. der Phys.* 1918, p. 81) describes experiments showing the drift of particles suspended in gases, to which phenomenon he ascribes the name photophoresis. In several respects, however, the above results are not entirely analogous. In his experiments he deals with individual particles in gases which drift directly parallel to the beam of light except for the gravity component. In air certain particles drift in the direction of the light-beam, *e. g.* gold and silver. These he terms light-positive. Others drift against the direction of the light (light-negative). In the present experiments the particles of gold and silver, as well as copper and gamboge, are light-negative. Again, in the very intense beam of the ultra-microscope, Ehrenhaft's velocities of drift in air are some five or ten times greater than the velocities of fall under gravity in the same medium, the velocity being proportional to the intensity of the light. The actual velocities he records are of the order of 10^{-4} cm./sec. This ratio of velocities is less than half that in the present experiments, the actual velocities being of the same order as those referred to in fig. 2; but if account be taken of the intensity of the light in the Tyndal Cone compared with that of a 100-c.p. lamp placed 20 cm. away, and also to the resistance motion experienced by the particle in air($\eta=2\times10^{-4}$) compared with that in water ($\eta=1\times10^{-2}$), it will be seen that the forces required to produce the velocities in the experiments are considerably greater than those he records.

It has been noticed by C. G. T. Morison (Proc. Roy. Soc. cviii. p. 280) that soils in suspension showed stratifications on exposure to light, in this case the light being in line with the camera and not at right angles to it as here. He found that the width of the stratifications depended on the colour of the light used; but, so far as I know, he has not published anything further on the question yet. The stratifications have their parallel, in the present work, in the sharp definition of the cloud-surface after exposure; but while in his case the stratifications are definitely created by exposure to light, in the present instance it is only a change of shape of an already existing cloud which takes place. The explanation of the sharp definition of the cloud-edge is not attempted here, but close observation of such a cloud leads one to the opinion that forces in the nature of surface tension of the cloud come into play at the transition from dense to clear solution.

Complete references to other observations on the action of light on the Liesegang phenomenon, including that by Hatschek (Proc. Roy. Soc. xcix. p. 496), are given by Morison in his paper.

My thanks are due to Professor A. W. Porter, D.Sc., F.R.S., for his help in the present work.

Carey Foster Laboratory,
University College, University of London.
13 July, 1926.

XCIII. *Werner's Co-ordination Theory and the Electrical Structure of the Atom. The Relationship between Valency and Co-ordination.* By S. H. C. Briggs, *D.Sc.*[*]

ALTHOUGH the electron theory of valency as developed by Thomson, Kossel, Lewis and Langmuir, Bohr, and others has given an almost complete solution of the valency problem so far as the simpler chemical compounds are concerned, it has not thrown much light upon the structure of the complex substances which were regarded by Werner as co-ordination compounds. The co-ordination compounds also include bodies of varying degrees of polarity, from the strongly polar *crystallized* sodium chloride on the one hand (Pfeiffer, *Zeitsch. anorg. Chem.* xcii. p. 376, 1915; xcvii. p. 161, 1916) to the typically non-polar carbon tetrachloride (Werner) on the other. Werner's co-ordination theory is the only *comprehensive* theory hitherto suggested which satisfactorily explains the structure of these various compounds. It is therefore highly desirable that Werner's theory of co-ordination and the electron theory of valency should be correlated. The object of the present paper is to determine the exact relationship between valency and co-ordination, and to show how Werner's theory of co-ordination can be derived from the electrical theory of atomic structure.

---

[*] Communicated by the Author.

WERNER'S THEORY.

A detailed account of the co-ordination theory is given in Werner's book, 'Neuere Anschauungen auf dem Gebiete der anorganischen Chemie' (3rd ed., 1913: Vieweg & Sohn Braunschweig) and also in the papers (*Zeitsch. anorg. Chem.* iii. p. 267, 1893; viii. pp. 153. 189, 1895). Werner regarded the affinity of an atom as an attractive force directed from the centre of the atom equally towards all parts of the surface of the atomic sphere. In Werner's own words ('Neuere Anschauungen,' p. 83): "Der bei gegenseitiger Bindung zweier Atome abgesättigte Affinitätsbetrag verteilt sich auf einen bestimmten kreisförmigen Abschnitt der Kugeloberfläche der Atome (Bindefläche) und wird mit der Natur dieser Atome in weiten Grenzen wechseln." Werner made a distinction between principal valency (Hauptvalenz) and subsidiary valency (Nebenvalenz). In platinic chloride $PtCl_4$ the chlorine atoms are attached by principal valencies. The platinum atom, however, is unsaturated and can combine by subsidiary valencies with two molecules of ammonia, to give the compound $Pt^{2NH_3}_{Cl_4}$, in which none of the chlorine atoms is ionizable, the ammonia molecules and the chlorine atoms all being in direct union (direktur Bindung) with the platinum atom. The addition of ammonia molecules in this manner is termed "Anlagerung" (apposition). The compound $Pt^{2NH_3}_{Cl_4}$ can react with a further quantity of ammonia, the chlorine atoms being successively displaced by ammonia molecules until the compound $(Pt6NH_3)Cl_4$ is obtained, in which all the ammonia molecules are in direct union with the platinum atom; but the chlorine atoms are now in an outer zone and are all ionizable, being in indirect union (indirekter Bindung) with the platinum. This process of displacement of chlorine atoms by ammonia molecules is termed "Einlagerung" (intercalation). In the compound $(Pt6NH_3)Cl_4$ the six molecules of ammonia together possess an amount of affinity equal to that of the platinum atom in $PtCl_4$, and the chlorine atoms are thus held in position in the outer zone (*Zeitsch. anorg. Chem.* iii. p. 324, 1893).

In the series of compounds $(Pt6NH_3)Cl_4$, $(Pt4NH_3Cl_2)Cl_2$, $(Pt3NH_3Cl_3)Cl$, $(Pt2NH_3Cl_4)$, $(PtCl_5NH_3)K$, and $(PtCl_6)K_2$, all of which are known, there are six atoms or groups, in every case in direct union with the platinum atom. Platinum is therefore said to have a maximum co-ordination number six. The maximum co-ordination number is defined by Werner as follows ('Neuere Anschauungen,' p. 58):—"Die maximale Ko-ordinationszahl muss als Raumzahl aufgefasst werden, d. h. als Zahlenbegriff, der angiebt, wievele Atome bestimmter Art sich in der ersten Sphäre eines anderen Elementaratoms räumlich anordnen können."

Werner showed that the maximum co-ordination numbers in the cases of different elements are either four, six, or eight. These numbers represent the apices of the three simplest regular polyhedra, thus emphasizing the essentially geometrical character of the conception of co-ordination, the co-ordinated atoms or groups being arranged symmetrically in space around the central atom.

ELECTRON THEORIES OF CO-ORDINATION COMPOUNDS.

The theory of valency of Lewis and Langmuir does not lead to any very definite conclusions with respect to co-ordination. As Langmuir has shown (J. Amer. Chem. Soc. xli. pp. 928–931, 1919), co-ordination compounds may equally well be regarded as electrovalency or covalency compounds.

The most interesting application of the electron theory of valency to co-ordination has been made by Sidgwick (J. Chem. Soc. cxxiii. p. 725, 1923). Sidgwick suggests that the element which acts as the central atom in the complex assumes the same external electron configuration as the inert gas which follows that element in the periodic table, each co-ordinated atom or group being united to the central atom by a bond of two electrons (covalency) such as is present in organic compounds. As examples, we may consider di- and trivalent chromium, di- and trivalent iron, and di- and trivalent cobalt, all of which give compounds with co-ordination number 6. Sidgwick's rule applies to the compounds of divalent iron and trivalent cobalt, but fails with trivalent iron, divalent cobalt, and all the chromium compounds. Since, however, the co-ordination number is 6 in all cases, it is reasonable to conclude that the *dominating* factor in the formation of co-ordination compounds is the tendency to produce spatially symmetrical structures, the actual co-ordination number being determined by geometrical considerations, in accordance with Werner's original views, and further that the formation of the electron configuration of an inert gas is a *subsidiary* factor only. When the two factors coincide, however, the compounds obtained possess a high degree of stability, and it was to such bodies rather than to co-ordination compounds in general that Sidgwick applied his theory.

Prideaux ('Chemistry and Industry,' xliv. p. 25, 1925) defines co-ordination compounds as compounds "whose formulæ . . . contain one or more mixed bonds." This definition appears to be inaccurate, as it excludes bodies such as SF_6 and CCl_4, which were regarded by Werner as typical, being co-ordinatively saturated ('Neuere Anschauungen,' p. 98).

It should also be observed that if in *all* co-ordination compounds the co-ordinated groups are linked to the central atom by two electrons equally shared, as suggested by Sidgwick and also by Lowry ('Chemistry and Industry,' xlii. pp. 318, 412, &c., 1923) and Brockman ('Chemistry and Industry,' xliii. p. 756, 1924), then co-ordination compounds in general should have a degree of stability comparable to that of organic compounds. This is by no means the case, many true co-ordination compounds being highly unstable. It would therefore appear that any *general* theory of co-ordination based upon the arrangement of electrons around the central atom must of necessity be extremely complicated and difficult. After a critical examination of Sidgwick's theory, J. D. Main Smith concluded ('Chemistry and Industry,' xliv. pp. 944, 1925):—"It appears probable that the maximum co-ordination number is totally unrelated to the size of any group or sub-group in any atom. The experimental evidence points to the conclusion emphasized by Werner that the co-ordination number is governed chiefly by the number of atoms that can be accommodated at the surface of the co-ordinating atom."

In the following pages it is shown that the co-ordination theory as originally established by Werner follows naturally with very slight modifications from the conception of an atom as a combination of electrons with a central positive nucleus. The point of view adopted is that of the theory of duplex affinity which I have developed in detail in previous papers (J. Chem. Soc. xciii. p. 1564, 1908; cxi. p. 253, 1917; cxv. p. 278, 1919; cxix. p. 1876, 1921; Phil. Mag. xlii. p. 448, 1921). A number of general conclusions are drawn with reference to the properties of co-ordination compounds, and in the concluding section the exact relationship between valency and co-ordination is discussed.

THE THEORY OF DUPLEX AFFINITY.

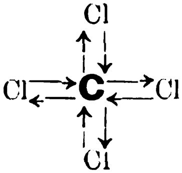
In the combination of potassium and chlorine to form potassium chloride, an electron is transferred from the potassium atom to the chlorine atom. Potassium is generally regarded as an element with positive affinity, and chlorine as an element with negative affinity. In terms of the electron theory we can therefore define positive affinity as a tendency to lose electrons, and negative affinity as a tendency to gain electrons.

The potassium atom which has lost an electron becoming a potassium ion has now a positive charge. But a positive charge attracts electrons, and therefore, by definition, the potassium *ion* has negative affinity, whereas the potassium *atom* has positive affinity. Similarly, the chloride ion which carries one negative charge has now a tendency to give up an electron to a positive charge, and therefore the chloride ion, by definition, has positive affinity.

We may describe the affinity of the atom as primary affinity and the affinity of the ion as secondary affinity, because the affinity of the ion is a secondary phenomenon which only appears after the affinity of the atom, that is to say the primary affinity, has come into action.

Potassium is therefore an element with primary positive affinity and secondary negative affinity, whereas chlorine is an element with primary negative affinity and secondary positive affinity, so far as the mutual relationship of the two elements is concerned.

The saturation of the affinity may be represented by an arrow pointing from positive to negative. Thus for the combination of potassium and chlorine we write $K \longrightarrow Cl$, the *thick* arrow indicating the passage of an electron from potassium to chlorine. The combination of the two ions $K^{\bullet}$ and Cl' to give a molecule may be written $K^{\bullet} \longleftarrow Cl'$, the arrow again pointing from positive to negative, but a *faint* arrow being used in this instance because no passage of electrons occurs. Combining the two formulæ, we have $\mathrm{K} \rightleftarrows \mathrm{Cl}$ for a molecule of potassium chloride. If the primary and secondary affinities are *equally* saturated, the formula must be written with two thin arrows pointing in opposite directions, since no transfer of electrons takes place in this case, which represents electron-sharing or non-polar union. As an example of a non-polar compound we may write carbon tetrachloride



Attention should now be directed to an important difference between secondary negative affinity and secondary positive affinity. Since atoms are incapable of interpenetration, each atom, so far as its effect on other atoms is concerned, may be regarded as a sphere with the nucleus at the centre. In a positive ion the charge is situated in the nucleus, and therefore, so far as the effect on other atoms is concerned, the attractive force due to this charge (the secondary negative affinity) may be regarded as distributed equally over the surface of the atomic sphere. A negative ion, on the other hand, has the charge on the electrons of the outer shell, and consequently secondary positive affinity is not distributed equally over the atomic surface. It may, indeed, be divided up equally among all the electrons of the outer layer as in a free negative ion such as Cl', but, on the contrary, it may also be confined to two electrons only, as in bodies such as $\mathrm{CCl_4}$ and $\mathrm{SF_6}$, in which each halogen atom is united to the central atom by a pair of electrons equally shared.

We see, therefore, that Werner's original conception of chemical affinity as an attractive force directed from the centre of the atom equally towards all points of the surface of the atomic sphere, applies in *all* cases with secondary negative affinity. The conception does not apply to secondary positive affinity in those instances in which the electrons are equally shared, as in $\mathrm{CCl_4}$. When the secondary positive affinity is divided up equally among all the external electrons, however, the general effect is equivalent to an attractive force emanating from the centre, which is Werner's conception (see Kossel, 'Valenzkräfte und Röntgenspektren,' 2nd ed. p. 15, 1924 : Julius Springer, Berlin).

It is significant that the majority of complexes have a positive atom at the centre. This is no doubt attributable to the fact that secondary negative affinity is *always* distributed equally over the surface of the atomic sphere in contradistinction to secondary positive affinity.

THE FORMATION OF COMPLEX COMPOUNDS.

From the truly non-polar character of carbon tetrachloride we may conclude that the geometrical conditions are such that the secondary affinities of the carbon and chlorine atoms are completely saturated. The case is different with platinum tetrachloride, the platinum atom (and therefore the chlorine atoms as well) being partially unsaturated. The platinum atom may consequently combine with two molecules of ammonia, the link being formed by electrons in the nitrogen octet, giving the compound $\mathrm{Pt}^{2\mathrm{NH}_3}_{\mathrm{Cl}_4}$, an example of the process called "Anlagerung" by Werner.

In the compound PtCl_4, and therefore also in $\mathrm{Pt}^{2\mathrm{NH}_3}_{\mathrm{Cl}_4}$, the chlorine atoms possess unsaturated secondary positive affinity, and will be attracted by the secondary negative affinity of the hydrogen in such molecules as water and ammonia. The attraction of the water molecules is not sufficiently great to cause the chloride ions to dissociate from the complex to any marked extent in the cold, freshly-prepared solution; but on boiling with a solution of ammonia, chloride ions are removed from the complex and their places taken by ammonia molecules—an example of Werner's process of "Einlagerung."

We may now consider the case of a strong electrolyte (a strongly polar compound) such as sodium chloride. In the isolated molecule NaCl, where the atoms are side by side, only a comparatively small portion of the surface of the atomic sphere of each ion comes under the immediate influence of the other ion. That portion of the atomic surface which is affected corresponds to Werner's "Bindefläche." The rest of the surface of each atomic sphere may be regarded as unsaturated. When such a molecule is dissolved in water the secondary negative affinity of the unsaturated sodium ion attracts the electrons of the oxygen in the water molecules, whereas the secondary positive affinity of the unsaturated chloride ion attracts the hydrogen nuclei of the water molecules. Water molecules therefore crowd round each ion (are co-ordinated round each ion), and in the course of thermal agitation the ions separate in the hydrated condition, the process being exactly as assumed by Werner.

In the vapour of sodium chloride, individual molecules are present, as shown by vapour-density determinations. When such a vapour cools down to the liquid and then to the solid state, since the ions are unsaturated in the individual molecules, the molecules will arrange themselves in such a manner that chloride ions surround the sodium ions, and sodium ions surround the chloride ions, giving finally a space-lattice built up of two kinds of interpenetrating complexes having the formulæ ($NaCl_6$) and ($ClNa_6$), as shown by X-ray analysis of the crystals. In other words, the compound crystallizes by polymerization, the new polymerized molecule comprising the whole crystal (see Phil. Mag. xlvii. p. 702, 1924).

When sodium chloride and platinic chloride react with each other, two chloride ions from the sodium chloride combine with each molecule of platinic chloride giving the compound Na_2PtCl_6, a further example of co-ordination. In the complex ($PtCl_6$) the central platinum atom has four positive charges, and the secondary negative affinity due to these charges is distributed over the surface of a comparatively small sphere. The complex is therefore markedly stable in solution. In the complex ($NaCl_6$) in the crystal of sodium chloride there is only one positive charge on the central atom, and, since the atomic volume of sodium is much greater than that of platinum, the secondary negative affinity due to this single charge is spread over the surface of a comparatively large sphere. The complex is therefore unstable and breaks up when the crystal is dissolved.

From these examples we see that co-ordination is involved in the solution and crystallization of strong electrolytes as well as in the formation of complex compounds.

In the formation of such a complex as $(Co6NH_3)^{+++}$ it should be observed that when the secondary negative affinity of the central atom is saturated by the secondary positive affinity of the nitrogen atoms, a corresponding amount of secondary negative affinity is liberated at the hydrogen nuclei. Hence, whereas the secondary negative affinity was distributed over the sphere of the cobalt atom in the ion Co^{+++}, in the complex ion $(Co6NH_3)^{+++}$ (assuming complete saturation of the Co) the same amount of affinity is now divided up among eighteen hydrogen atoms which must be regarded as lying on the surface of a much larger sphere. This is in strict accordance with Werner's original theory, in which the charge was supposed to be distributed over the surface of the complex ion. We might therefore expect to find that additional molecules of ammonia can be added to the complex $(Co6NH_3)^{+++}$, and that these will arrange themselves outside the six already present and be much less firmly attached than the first six. Such compounds have been quite recently prepared by Ephraim (*Zeit. anorg. Chem.* cxlvii. p. 25, 1925), who finds that the substance having the formula $(Co6NH_3)Cl_3, 6NH_3$ decomposes at $-24°$.

Lowry ('Chemistry and Industry,' xlii. pp. 316, 412, 462, &c., 1923) has suggested that in a negative complex such as $(PtCl_6)^{--}$ the two negative charges are situated on the central atom, *i. e.* on the most electropositive atom in the complex. This somewhat remarkable conclusion results from the assumption that each chlorine atom is united to the platinum by a pair of electrons *equally* shared. Electrons need not always be shared equally, however (Fajans, *Naturwissenschaften*, xi. p. 165, 1923; Knorr, *Zeitsch. für anorganische und allgemeine Chem.* cxxix. p. 109, 1923; Briggs, Phil. Mag. xlvii. p. 702, 1924); and if the sharing is such that the secondary negative affinity of the platinum atom is fully saturated, each chlorine atom will then be left with some unsaturated secondary positive affinity. Chlorine atoms in this condition will be attracted by the hydrogen nuclei of water molecules in aqueous solution, and will therefore exhibit some slight tendency to dissociate from the complex being replaced by water. I showed some years ago that such very stable complexes as the ferrocyanide and the ferricyanide ions are dissociated in this way, their solutions containing a small amount of the corresponding aquopentacyano-complex (J. Chem. Soc. cxvii. p. 1026, 1920). The charge in the negative complexes would therefore appear to be distributed over the surface of the outer zone in accordance with Werner's theory rather than in the central electropositive atom as assumed by Lowry.

From the considerations put forward in this and the preceding sections of the present paper, it is seen that complex compounds are formed as the result of the action of secondary affinity, whereas the simpler binary compounds arise from the action of primary affinity. As the various electron theories of valency deal essentially with primary affinity phenomena, it is not surprising that they are of so little aid in elucidating the structure of complex compounds. It also follows that primary and secondary affinity correspond to Werner's Haupt- and Nebenvalenz (principal and subsidiary valency); but whereas Werner's two types of valency did not differ in sign, as we have already seen, it follows from the electron theory that primary and secondary affinity are opposite in sign. The difference between Werner's Haupt- and Nebenvalenz is never very clear, and disappears entirely in such a compound as $K_2(PtCl_6)$, in which all the chlorine atoms are equal. It should therefore be noted that if we ignore the passage of electrons and regard all compounds as being built up of ions rather than atoms, the difference disappears from the electron point of view exactly as with Werner's theory.

Seeing that the secondary affinity of the central atom in a complex is distributed equally over the surface of the atomic sphere, it follows that for maximum saturation the co-ordinated atoms or groups must be arranged symmetrically in space around the sphere. We therefore have the maximum co-ordination numbers referred to above, to which should be added the number 2 as the co-ordination number of hydrogen, in view of Lowry's work (Lowry and Burgess, J. Chem. Soc. cxxiii. p. 2111, 1923).

THE PROPERTIES OF COMPLEX COMPOUNDS.

The principles put forward in this paper make it possible to deduce some general rules with reference to the properties of complex compounds. Some, though not all of these rules, have been mentioned in the previous papers referred to above, but they are brought together for the first time in a complete form.

(1) Since the limiting case of the strongest possible electrolyte may be represented by the formula $A \longrightarrow B$, and a non-electrolyte by $A \rightleftarrows B$, it follows that, if we diminish the secondary affinity bond in any compound AB, the tendency to electrolytic dissociation will be increased. The secondary affinity bond may be diminished by building a complex around A or B, because, as we have seen above, in the complex the secondary affinity is distributed over a much larger spherical surface than in the simple binary compound, and the attractive force on the "Bindefläche" will be correspondingly decreased. We therefore have the general rule that

A complex electrolyte is a stronger electrolyte than the simple electrolyte from which it is derived . . . (1)

Examples:—The weak bases $Ni(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$, &c., by combination with ammonia give complex bases as strong as the alkalies, and the extremely weak acid HCN gives the very strong complex acids $H_3(Co(CN)_6)$, $H_3(Fe(CN)_6)$, $H_4(Fe(CN)_6)$, &c.

(2) In a series of compounds AB, $AB_2 \ldots AB_x$ the charge on A increases with increase in valency. Therefore as the valency increases, the secondary negative affinity of A increases also, until we finally reach a stage in which it is sufficiently strong to pull an electron out of an anion B. A limit is thus placed to the value of x and to the valency of A. If, however, we saturate part of the secondary negative affinity of A by building up a complex around A, we can then increase the value of x. We therefore have a general rule to the effect that

> *In the highest valencies of an element the complex compounds are more stable than the simpler compounds from which they are derived* . . . . (2)

As examples it may be noted that although $CoCl_3$ cannot be prepared, $(Co6NH_3)Cl_3$ is a very stable substance, and that the plumbichlorides are a very well-defined class of compounds, although $PbCl_4$ is highly unstable. The only exceptions to this rule appear to be the compounds of *o*-phenanthrolin and α dipyridyl with ferric salts (Werner, 'Neuere Anschauungen,' p. 66), which easily change into ferrous compounds, possibly owing to the action of Sidgwick's rule, referred to above (p. 1028).

(3) The stability of the higher valencies may also be increased in another manner. In weak acids the secondary affinities are more fully saturated than in strong acids, the limiting case of the strongest possible acid having the formula $H \longrightarrow X$, whereas the weakest possible acid would be non-polar, as shown by the formula $H \overset{\dashrightarrow}{\longleftarrow} X$. Consequently in the salts of weak acids the secondary negative affinity of the metal will be more fully saturated than in the salts of strong acids, from which it follows that

> *In the highest valencies of a metal the salts with weak acids have a tendency to be more stable than the salts of strong acids* . . . . (3)

This explains why it is possible to prepare solutions and derivatives of cobaltic acetate but not of cobaltic chloride. A significant exception to the rule is found in ferric cyanide, which loses some cyanogen with the greatest ease. If ferric cyanide has the formula suggested in a former paper (Trans.

Chem. Soc. cxvii. p. 1028, 1920), it is possible that this exception is also due to the working of Sidgwick's rule *.

(4) Owing to the increase of the secondary negative affinity of a metal with increase in valency, it follows that

> *With increase in valency the maximum co-ordination number tends to increase, and in those cases where the co-ordination number does not increase the complex compounds are the more stable the greater the valency of the central atom* . . . . (4)

As examples we find that platinum in the platinous salts has co-ordination number four, and in the platinic salts co-ordination number six, and also that in the cobaltic compound $(Co6NH_3)Cl_3$ the ammonia molecules are much more firmly attached than in the corresponding cobaltous compound $(Co6NH_3)Cl_2$.

(5) Consider a series of hydroxides M . OH, $M(OH)_2$, &c. Since the secondary negative affinity is spread equally over the surface of the atomic sphere, the attractive force increases at every point of the atomic surface with increase in valency of the central atom. Therefore as we pass from M(OH) to $M(OH)_2$, not only do we add a second hydroxyl group, but the first hydroxyl group is more firmly attached in the dihydroxide than in the monohydroxide, because of the increase in the secondary negative affinity of that part of the surface of M which comes under the influence of the first hydroxyl. Consequently, as the valency of M increases, the oxygen atoms become more and more firmly attached. But as the secondary negative affinity of the oxygen is increasingly taken up by the central atom, the intensity of the bond between the oxygen and the hydrogen ion is diminished. Therefore

> *As the valency of an atom increases, its hydroxides tend to become decreasingly basic or increasingly acidic.* (5)

The compounds of manganese and the oxy-acids of nitrogen and of chlorine are well-known examples of this rule (compare Trans. Chem. Soc. cxv. p. 287, 1919).

(6) Again, in any series of compounds AB, AB_2 ... AB_x, where A is a positive element and B is a negative element, as we pass along the series the B ions become more and more firmly attached with increase in the valency of A, as shown

---

* Alternatively, the case may be similar to that of $Cu(CN)_2$ and $Cu(NO)_2$, the instability of which has been explained by Fajans (*loc. cit.*).

in the last paragraph. It therefore follows that

> *The polar properties of the members of a series* AB, AB_2... AB_x *decrease with increase in valency of the central atom.* . . . . (6)

Many examples are found in the metallic halides: thus $SnCl_2$, $SbCl_3$, and VCl_3 are solids, whereas $SnCl_4$, VCl_4, and $SbCl_5$ are liquids at the ordinary temperature.

(7) Since secondary negative affinity is distributed equally over the surface of the atomic sphere, the optimum conditions for complete saturation of the secondary negative affinity of the central atom will be attained when the co-ordinated atoms are sufficiently numerous to influence directly all parts of the atomic surface of the central ion, and when they can be distributed symmetrically in space around the central ion. Consequently

> *Compounds of the type* AB_x *will be most likely to exhibit non-polar properties when* $x=4$, 6, *or* 8, *corresponding to arrangement of the* B *atoms around the* A *atom at the corners of a regular tetrahedron, a regular octahedron, and a cube respectively.* . . . . . . (7)

Examples:—CCl_4, RuO_4, OsO_4, SF_6, WF_6, and OsF_8. (See Trans. Chem. Soc. cxv. p. 281, 1919.)

(8) *If the salts of a metal combine with ammonia or other co-ordinating substance, the avidity will be greater with the salts of strong acids than with the salts of weak acids.* . . . . (8)

(See Trans. Chem. Soc. cxi. p. 263, 1917.)

THE FUNDAMENTAL CHARACTER OF THE CO-ORDINATION PROCESS, AND THE RELATION BETWEEN VALENCY AND CO-ORDINATION.

The atom of an alkali metal consists of a positive ion with one electron revolving around it. At any given instant, therefore, only a part of the surface of the atomic sphere of the positive ion comes under the direct influence of the electron, and the alkali metal, lithium for example, may be regarded as a strongly polar compound analogous to potassium chloride. Writing lithium as a compound of a kernel and an electron, we have Li^kE, Li^k being the lithium kernel and E the electron. As we pass along the series from lithium to neon, we continually increase the charge on the kernel and at the same time we add electrons. In accordance with rule

6 above therefore, as we pass along the series from lithium to neon, the valency electrons should become more and more firmly attached, and the polar properties (that is to say, the electropositive character) of the atom should diminish. This is actually the case, neon having the properties of an ideally non-polar substance.

Further consideration must now be given to the polar character of the metals. From the researches of Kraus (J. Amer. Chem. Soc. xxx. p. 1323, 1908; xxxvi. p. 864, 1914; xliii. p. 749, 1921) it may be concluded that, when an alkali metal is dissolved in liquid ammonia, the ammonia molecules are co-ordinated around the ion of the metal, and dissociation takes place in accordance with the equation; for example,

$$K^kE + xNH_3 = K^k xNH_3 + E$$

$$\text{(or } (KxNH_3)^{\bullet} + E, \text{ since } K^k = K^{\bullet}),$$

the free electrons also becoming solvated.

A similar process takes place if the solvent is metallic mercury, because Coehn and Duhem (*Zeitsch. Physik*, xxvii. p. 358), by a study of the electrification produced in gases by bubbling through pure mercury and through mercury containing sodium, obtained evidence of the existence of complex ions $(NaHg_x)^{\bullet}$ *.

In exactly the same way, when potassium is dissolved in water the water molecules are co-ordinated around the potassium ions as explained above (p. 1032), and dissociation into hydrated potassium ions and electrons takes place. The electrons then decompose the water with the formation of hydroxyl ions and hydrogen. If a piece of a less electropositive metal is placed in water, in the course of thermal agitation a few positive ions at the surface, under the attraction of the oxygen of the water molecules, will become sufficiently detached to undergo complete co-ordination, and will be carried away into the solution as hydrated ions. In such a metal, however, the positive ions have a greater charge and a smaller atomic volume than the ions of the alkali metals; the electrons are therefore held more firmly in the metal, and the excess of electrons after removal ot the hydrated positive ions remain as a layer of negative electricity on the surface of the metal, being held in position by the attraction of the positive ions near the surface.

---

* A compound such as $NaHg_6$ would therefore appear to be an *electride* of a complex sodium mercury base, and the formula should be written $(Na^kHg_6)E$ (compare Phil. Mag. xlii. p. 448, 1921). Other evidence in support of this formula with mercury atoms co-ordinated around the sodium ion is obtained from the recent work of Kraus (J. Amer. Chem. Soc. xlvii. p. 43, 1925), who found that although sodium plumbides and tellurides in which the lead and tellurium are present as anions are readily soluble in liquid ammonia, the compounds of sodium and mercury are insoluble; and this is just what might be expected if the secondary negative affinity of the sodium ion were already saturated by the electrons of the co-ordinated mercury atoms, as in the formula $(Na^kHg_6)E$ (or $(NaHg_6)^{\cdot}E$). Other substances which may also be regarded as electrides are the compounds of metals with ammonia and with organic bases such as calcium ammonia $(Ca6NH_3)^{\cdot\cdot}E_2$ and sodium pyridine $(Na2C_5H_5N)^{\cdot}E$, and the free radicles, *e.g.* the monomeric form of tetraethylammonium $(NEt_4)^{\cdot}E$ of Schlubach and Ballauf (*Ber. der deutsch. chem. Gesellsch.* liv. p. 2811, 1921). Bodies with such a feebly-bound electron are naturally very unstable and reactive, sodium pyridine, for example, being spontaneously inflammable in the air (Emmert, *Ber. der deutsch. chem. Gesellsch.* xlvii. p. 2598, 1914; xlix. p. 1060, 1916).

It would appear from these considerations that co-ordination is deeply involved in the phenomena observed when metals are immersed in an ionizing solvent such as water. The actual process that takes place, from this point of view, is a solution of positive ions from the surface of the metal due to an attraction exerted by the molecules of the solvent, rather than to a force driving the ions outward from the metal, an electrolytic solution *pressure*. It may be observed that Langmuir has objected to the conception of a solution pressure on other grounds (J. Amer. Chem. Soc. xli. p. 877, 1919; *cf.* Pisarzhevskii, J. Russ. Phys. Chem. Soc. liv. p. 778, 1924).

We have now seen the co-ordination process at work in the formation of complex salts, in the solution and crystallization of strong electrolytes, and in the phenomena of electrolytic "solution pressure." The field of action of the co-ordination process extends, however, into the subatomic region as well. According to the modern theories of atomic structure, the electrons or their orbits are arranged around the central positive charge with a high degree of symmetry, and it is significant that the maximum number of electrons in the subgroups of Bohr are 2, 4, 6, or 8—the same as the maximum co-ordination numbers given above, viz. Werner's numbers with the addition of 2 for hydrogen as suggested by Lowry.

Now, if we write potassium and chlorine as compounds of kernels and electrons, the formation of potassium chloride is given by the equation:

$$K^kE + Cl^kE_7 = K^k(Cl^kE_8),$$

with potassium chloride as an *electron co-ordination compound*, the reaction being analogous to the formation of potassium platinichloride:

$$2KCl + PtCl_4 = K_2(PtCl_6).$$

In an earlier paper (Phil. Mag. xlii. p. 448, 1921) it was shown that all types of chemical compounds may be represented in this manner, their formation being due to the co-ordination of electrons (or electron orbits), so that, in the ultimate analysis, all valency phenomena are based upon co-ordination. It therefore follows that co-ordination, that is to say the symmetrical arrangement in space of electrons (or electron orbits), ions, or molecules around a central kernel or ion, is the fundamental plan according to which all chemical structures are built up.

The relation between valency and co-ordination may also be demonstrated in another way. Suppose, for example, that a number of simple cyanides had been isolated in the pure condition and their combinations with each other had been studied, but that nothing were known with regard to the atoms of which they are composed. Let $a=\mathrm{KCN}$, $w=\mathrm{AgCN}$, $x=\mathrm{CuCN}$, $y=\mathrm{Fe(CN)_3}$, and $z=\mathrm{Fe(CN)_2}$. Then $\mathrm{K(Ag(CN)_2)}=aw$, $\mathrm{K(Cu(CN)_2)}=ax$, $\mathrm{K_2(Cu(CN)_3)}=a_2x$, $\mathrm{K_3(Cu(CN)_4)}=a_3x$, $\mathrm{K_3(Fe(CN)_6)}=a_3y$, and $\mathrm{K_4(Fe(CN)_6)}=a_4z$. We thus obtain what correspond to ordinary valency formulæ for the co-ordination compounds in question; and if a is regarded as monovalent, then w is also monovalent, x is mono-, di-, or trivalent, y is trivalent, and z is tetravalent. Consequently, if the simpler molecules are taken as the units of structure, only valency formulæ are obtained. On the other hand, we have seen above that if the electrons and kernels are regarded as the units, all formulæ become co-ordination formulæ. In chemistry, however, it is customary to take as the units of structure the atoms which represent an intermediate stage between the simpler molecules on the one side and the kernels and electrons on the other. This leads us to the final conclusion that any system of formulating chemical compounds based on the atom as the unit must, of necessity, include both valency formulæ and co-ordination formulæ; and consequently that attempts to devise valency formulæ for the compounds with a co-ordination complex are doomed to failure, a system of valency based upon the atom to include *all* compounds being, in the nature of the case, an impossibility.

April 10th, 1926.

XCIV. *The Flash Arc Spectrum of Potassium.* *By* F. H. NEWMAN, *D.Sc., A.R.C.S., Professor of Physics, University College of the South-West of England, Exeter* *.

[Plate XX.]

1. *Introduction.*

THE author has described previously † the excitation of enhanced lines in an interrupted arc passed between sodium-potassium alloy electrodes, the arc lines being extremely faint. The appearance of enhanced lines in the arc is of common occurrence, particularly at that part of the arc in the vicinity of the electrodes, but, as a rule, they are faint. Their great relative intensity in the interrupted arc was attributed to the relatively high potential fall which operated when the arc was started. The electric force in the vicinity of the electrodes, particularly the cathode, is great, and the electrons in these parts may acquire impacting energy between successive atomic collisions sufficient to doubly ionize the metallic atoms, thus giving rise to the enhanced lines. This phenomenon occurs only at low pressures when comparatively few electronic-atomic collisions take place over the short accelerating field constituting the cathode potential fall. The latter must be greater than the minimum voltage through which an electron must fall in order to ionize the surrounding vapour atoms, but it is not always the ionizing potential. If the vapour is non-atomic it is probably identical with the first resonance potential, or the difference between the first resonance potential and the ionizing potential. Although no accurate measurements of the thickness of the region of the cathode fall in arcs have been made, theoretical considerations indicate that it should be about equal to the mean free path of the electrons from the cathode, since they are likely to ionize at first impact, as the electric intensity diminishes with distance from the cathode.

In the case of potassium there are two ways in which the atom may be doubly ionized. The outermost electron may be removed first by impacting energy equal to 4·32 volts, followed by a second collision ejecting an electron from the M ring. On the other hand, the electron from the M ring may be ejected first by the requisite energy—23 volts ‡.

---

* Communicated by the Author.

† Phil. Mag. i. p. 721 (1926).

‡ Mohler & Foot, Bur. of Standards Sci. Paper No. 425 (1921).

The work necessary to remove the second electron from its orbit in the singly ionized atom is 11·5 volts, so that the complete spark spectrum of potassium requires for its excitation the removal of one M electron corresponding to energy 23 volts followed by impacting energy of 11·5 volts through which the outer electron is removed. The complete spark spectrum will therefore make its appearance when the energy is equivalent to 34·5 volts, although the enhanced lines should begin to appear if the impacting energy has a value greater than 23 volts, when the second electron is displaced to an outer orbit but not necessarily ejected from the atom.

In a similar manner it may be proved that the enhanced lines for most elements should appear when the impacting energy is below 50 volts, so that these lines may be expected to occur under favourable conditions in the ordinary arc discharge. Although they do sometimes appear in this manner they are, as a rule, faint, because the actual potential difference across the arc, when the latter is passing, is small, and unless the pressure is very low the mean free path of the electrons is small, so that the accelerating voltage per mean free path of the impacting electron is also likely to be very small. It is evident, however, that in the case of a flash arc at low pressures, *i. e.* an arc which is intermittent, the actual potential difference between the electrodes at each flash or, at any rate, for a period of the duration of the flash, will be the full applied voltage, and if the vapour pressure is maintained at a very low value, conditions are favourable for an appreciable fraction of the electrons to attain energy equivalent to that necessary for the production of the enhanced lines of the vapour. This theory has been tested in the following manner.

2. *Experiments.*

A vacuum arc discharge-tube contained two potassium electrodes, the potassium being packed into glass tubes through which passed iron rods by means of which the voltage was applied. These potassium electrodes were distant apart 5 mm., and a third iron electrode was inserted in the tube so that a momentary electric discharge from a coil could be passed through the tube to start the arc. No external heating was applied. By means of a rotating commutator the arc, when once started, could be quenched and struck alternately, and if the time interval between make and break was small—less than a second—the arc would persist in this intermittent manner. It was assumed that the full applied potential difference, 120 volts, was operative for at least an appreciable period of the time interval tha the arc was in existence. The tube was connected to a pump which, running continuously, maintained the pressure below 10^{-3} mm. of mercury. One end of the tube was closed by means of a quartz window and light from the potassium cathode was focussed directly on to the slit of a quartz spectrograph, the resulting spectrum being photographed on panchromatic plates with an iron comparison spectrum. The spectra obtained in this manner consisted almost entirely of enhanced potassium lines, the arc lines being very faint in comparison, as shown in Plate XX. The chief lines were measured and are given in Table I. No lines appeared below $\lambda = 2986$ Å.U. Most of the lines measured occur in the spark discharge obtained by passing a powerful electrodeless discharge through low density vapour.

TABLE I.

The "flash" arc spectrum of Potassium.

Wave-length, λ Å.U.	Intensity.
6307	3
6247	2
6120	4
5479	0
5464	0
5056	2
5005	4
4829	6
4660	2
4642	2
4608	5
4596	0
4505	5
4467	3
4454	4
4424	1
4388	5
4365	4
4340	4
4309	6
4305	4
4288	1
4263	6
4226	6
4223	6
4210	2
4202	1
4186	8
4149	4
4135	4
4115	5
4094	6
4058	3
4025	3
4012	2
4009	1
4001	4
3995	4
3967	3
3963	2
3955	3
3943	4
3924	3
3920	3
3898	5
3878	1
3874	1
3862	5

TABLE (*continued*).

Wave-length, λ Å.U.	Intensity.
3818	8
3801	6
3783	4
3767	3
3745	0
3739	1
3722	2
3716	0
3682	4
3676	3
3669	2
3636	1
3627	0
3618	5
3609	4
3555·4	0
3548·3	0
3531·0	8
3517·5	0
3479·4	0
3475·2	0
3440·4	3
3434·7	2
3422·3	1
3404·6	6
3392·4	1
3385·3	5
3381·0	5
3374·0	5
3363·2	7
3364·4	3
3358·2	2
3345·6	5
3324·4	1
3312·8	3
3292·1	3
3279·2	1
3262·1	1
3260·3	0
3257·3	1
3244·3	1
3223·5	1
3220·6	2
3209·4	1
3202·0	2
3190·0	3
3170·0	2
3159·2	1
3148·0	1
3129·6	3
3105·1	4
3077·0	1
3062·1	5
3057·6	0
3053·1	1
3035·0	1
3031·9	1
3024·6	1
2993·4	2
2986·0	1

The configuration of the singly-ionized potassium atom resembles that of the normal argon atom, and it is to be expected therefore that the enhanced spectrum of potassium should resemble in type that of the ordinary arc spectrum of argon. McLennan * has shown that such is the case. Argon emits two types of arc spectra, the red spectrum at moderate excitation and the blue one when intense stimulation is used. McLennan found that the enhanced lines of potassium fell approximately into two divisions with a certain amount of

* Proc. Roy. Soc. A, 100. p. 182 (1922).

overlapping. In the first division, which corresponds with the argon red spectrum, the centre was approximately at $\lambda = 3800$ A.U., and in the other, corresponding to the blue argon spectrum, the centre was at $\lambda = 2100$ A.U. As stated above, in the present work no lines below $\lambda = 2986$ A.U. were observed, so that the spectrum obtained is analogous to the argon red spectrum. This is to be expected when one considers the low excitation voltage used in the experiments, and this result still further emphasizes the similarity, suggested by Sommerfeld, between the normal argon atom and the singly-ionized potassium. Unfortunately the complexity of the argon arc and the potassium spark spectra has prevented this parallelism from being established numerically in a satisfactory manner.

The author wishes to express his thanks to the Royal Society for a Government Grant which enabled this research to be carried out.

XCV. *Researches on the Electric Discharge in Gases and the accompanying Radiation.* *By* A. Dauvillier, *Dr. ès Sciences* *.

(I.) *Pressure Effects.*

In a former paper † an hypothesis was put forward to explain the sharp cathodic edge of the negative glow. According to this theory, differences of pressure should exist in the discharge. We have investigated this effect by passing a narrow beam of soft X-rays transversely through the discharge, differences of opacity of the gas being an indication of pressure variations.

The apparatus, in "pyrex" glass, comprised three parts (fig. 1): the X-ray tube (hot cathode), the discharge tube, and the low-pressure ionizing chamber, for measuring the radiation intensities, separated by very thin celluloid films, which were vacuum tight and of the order of a wave-length of light in thickness. Both the X-ray and discharge tubes were run on a voltage of about 400. The discharge-tube electrodes were movable (magnetic device) so that it was possible to explore any portion of the discharge by means of the X-ray beam.

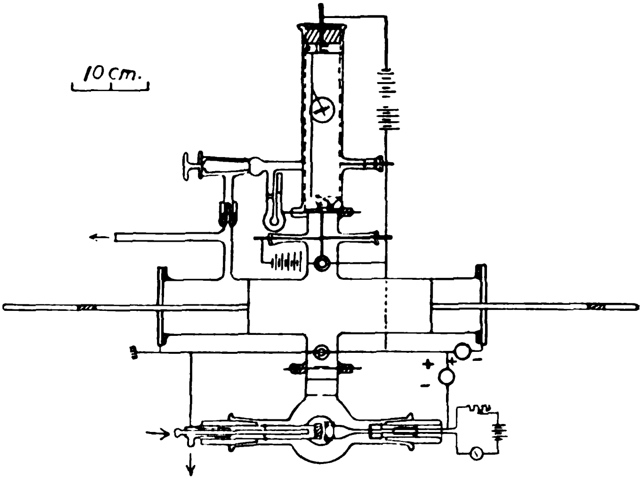
---

* Communicated by the Author.

† *Comptes Rendus,* 181. p. 601 (1925).

The gases used were He, Ne, and A, at pressures varying from about 0·1 to 3 mm. Since the intensity of the radiation of the discharge was of the same order as that of the X-rays, this intensity was measured first, that of the combined X-rays and discharge secondly, and that of the X-rays alone thirdly. A comparison of the difference of intensities (2) and (1) with the intensity (3) for the X-rays alone gave an indication of the pressure effect. This effect proved to be feeble, being masked by the presence of a large number of neutral atoms. It was clearly greater (three times) than the possible experimental error only in one point, namely, the sharp cathodic edge of the negative glow, proving the existence of a very considerable density of positive ions. It was always found at this point, located in a thin layer of gas of ½ mm. or less in thickness. A much feebler effect of the same kind was also found at the cathodic edge of the positive column. In no part of the discharge were depressions observed, and these are probably located over large areas, like the Faraday Dark Space. The expected depression in the Crookes Dark Space would appear to have been masked by the double gas current which flows into it. The general trend of the experiments appeared to be in favour of the above.

Fig. 1.

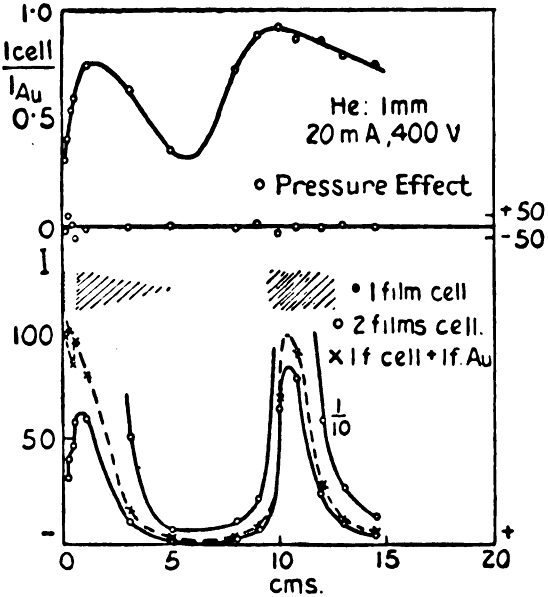


(II.) *Radiations from the discharge.*

These radiations, discovered by Wiedemann, were studied by Sir J. J. Thomson *, who arrived at the conclusion that they were of two types : the very absorbable radiation of Schumann, and penetrating X-rays corresponding to the quantum of the voltage applied to the discharge tube.

We have studied the radiation for the different parts of the discharge, characterizing their quality by the filtration exercised by screens—a film of celluloid and a gold-leaf (beaten gold)—placed (magnetic device) in the path of the beam of radiation. Standardization of the radiations was carried out by the X-ray tube running at different voltages. The radiation was in general located in the visible parts of the discharge (fig. 2), with the exception of the Crookes Dark Space, where it is noteworthy. The positive glow invariably consisted of Schumann radiations, the intensity being proportional to the current and independent of the voltage. The quality of the radiation emitted by the negative glow was found to depend, at constant voltage, upon the pressure (fig. 3). When this was of the order of a mm., radiations of a Schumann-Lyman type alone were

Fig. 2.

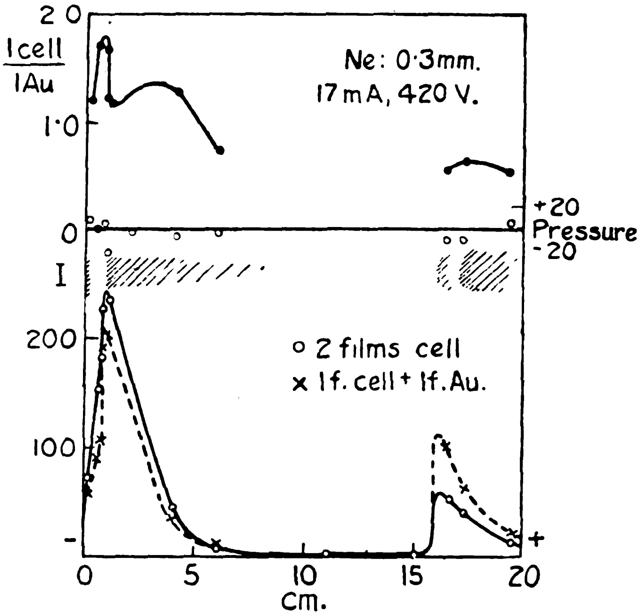


---

* Phil. Mag., July 1924 and May 1925.

observed, but at pressures of about $\frac{1}{10}$ mm. there appeared intense characteristic X-rays of short wave-length, such as the L rays of argon, characterized by their quality and critical potential of excitation (fig. 4). The Crookes Dark Space radiation was remarkable—very soft just in front of the cathode and increasing in penetration towards the edge of the negative glow where it increased brusquely and discontinuously. It thus appears to be due solely to the electrons from the cathode. The negative glow would thus appear as a gaseous anticathode of an X-ray tube with similar laws of emission.

Fig. 3.



We have not found any appreciable amount of independent Röntgen radiation in the negative glow, as was found in the experiments of Sir J. J. Thomson. The comparison effected by means of the X-ray tube has shown that if this type of radiation exists it is considerably less than that emitted by a solid body *.

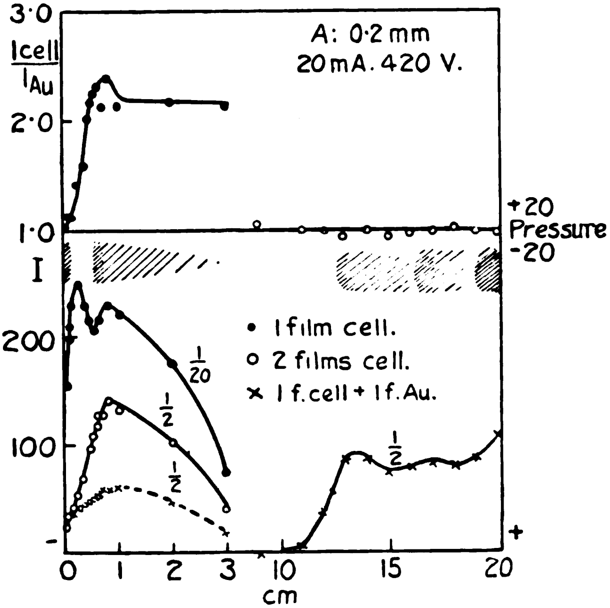
---

* On the contrary, the Schumann-Lyman radiation, which is emitted with very great efficiency by free atoms, is very feeble in the radiation of the solid target. This radiation is responsible—by its photoelectric effect on the cathode—for the *general* cathodic stream (which causes the negative glow) and for the appearance of arc in the thermo-ionic discharge at low potential through gases at very low pressure.

(III.) *The Nature of Soft X-Rays.*

The standardization of the radiations of the discharge naturally led to a study of the nature of the soft Röntgen rays emitted by the X-ray tube. Different authors * had already shown that these formed both qualitatively and quantitatively a continuous spectrum, independent of the nature of the anticathode and devoid of characteristic rays. This result is in opposition to the laws governing X-ray emission in the field of spectrography. We have, on the contrary, observed that these rays contained intense characteristic radiations and that they depended largely upon the nature of the anticathode, exhibiting clear discontinuities. Experiments were made with anticathodes of carbon and tungsten. The former showed (fig. 5) emission of K-radiation at 295 volts. For example, at 340 volts the K radiation of carbon was *at least* three times the intensity of the general radiation. These results were verified by the absorption experiments.

Fig. 4.

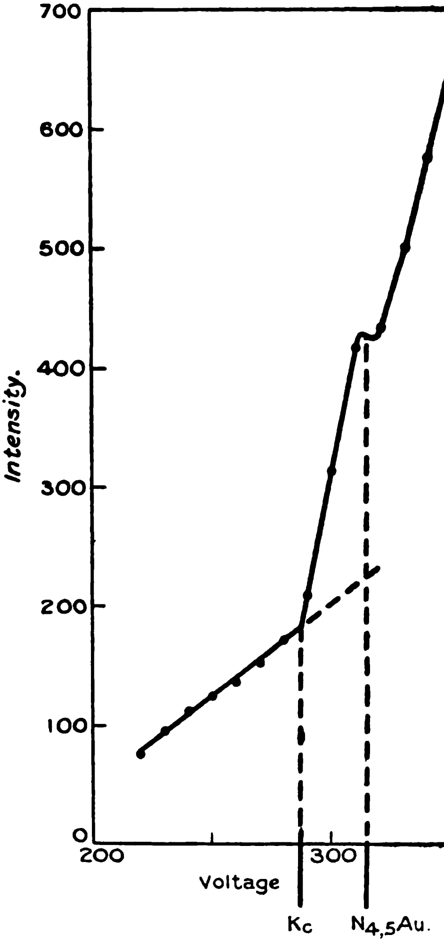


---

* *Cf.* Holweck, *Thèses* (Paris, 1920).

We observed, with a tungsten target, many discontinuities which disappeared (fig. 5, lower curve) when the gas pressure in the tube attained a bar and that the output often dropped to a quarter of the normal value for much lower pressures.

Fig. 5.



Ionization-volts graph showing K emission spectrum of carbon N_4, absorption edge of gold.

This appears to be due to the adsorption on the anode of gas layers which change the intensity of secondary cathode rays impinging on the celluloid window.

The nature of soft X-Rays was later definitely proved by obtaining their spectra: the Kα lines of oxygen (24 Å.), carbon (43·5), and boron (70) *.

The author wishes to express his indebtedness to Dr. J. Taylor, Rockefeller International Fellow, for his constant and helpful assistance during all the course of the work.

Laboratoire de Recherches Physiques,
sur les Rayons X, Paris.

XCVI. *A Simple Exposition of Electromagnetic Relations.* *By* H. F. Biggs, *M.A., M.Sc., Demonstrator in Physics, Oxford University* †.

THE following derivation of the circuital theorems on which Maxwell's equations depend has been developed from the teacher's point of view, but it presents perhaps some points of physical interest.

Now that the objective existence of point-charges has been a familiar idea for a quarter of a century, simplifications may well be made in the exposition of electromagnetic theory by basing it on the fundamental law of the force on a charge moving in a magnetic field. This law is the simplest electromagnetic relation, involves no limits or approximations, is universally true‡, and is directly verified by experiment with considerable accuracy. I doubt if any one stage of the reasoning is new, though many of the arguments are in the converse of the usual order, but I have not been able to find that the scheme has been presented as a whole before.

Fundamental Relation.

The force on a charge e e.s.u. moving with a velocity $\mathbf{v}$ cm./sec. in a field $\mathbf{H}$ gauss is

$$\mathbf{F}=\frac{1}{c}e\mathbf{v}\times\mathbf{H}\text{ dynes. . . . . . . (1)}$$

---

* *Comptes Rendus*, 182. p. 927 (Avril 1926); *Bulletin, Sté. fr. Sc. Phys.* (7 Mai, 1926).

† Communicated by the Author.

‡ Apart from quantum mechanics.

Mutual Action between Charge and Pole in Relative Motion.

If $\mathbf{H}$ in (1) be due to a pole m at a distance r from e, we put $\mathrm{H}=m/r^2$ and get for the magnitude of the force on e or on m the symmetrical expression

$$\mathrm{F}=\frac{v}{c}\frac{em\sin\theta}{r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where θ is the angle between $\mathbf{r}$ and $\mathbf{v}$; the direction of the forces is perpendicular to $\mathbf{r}$ and $\mathbf{v}$.

This may, of course, be written in vector notation

$$\mathbf{F}=\pm\frac{1}{c}em\,\mathbf{v}\times\nabla\frac{1}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

Now putting $e/r^2=\mathrm{E}$, the electric intensity at m, we find for the force on m

$$\mathbf{F}=\frac{1}{c}m\mathbf{v}\times\mathbf{E}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$\mathbf{v}$ being still the velocity of e relative to m.

Supposing that e as it moves carries its own field with it, and also that it is only relative motion that matters, we may divide (1) by e and (3) by m, obtaining for the electric intensity due to a moving magnetic field

$$\mathbf{E}=-\frac{1}{c}\mathbf{v}\times\mathbf{H}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and for the magnetic intensity due to a moving electric field

$$\mathbf{H}=\frac{1}{c}\mathbf{v}\times\mathbf{E}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $\mathbf{v}$ is now in each case the velocity of the field relative to the point considered.

The electromotive force between two near points in a moving magnetic field is then

$$\begin{aligned}\mathbf{E}\,.\,\mathbf{ds}&=-\frac{1}{c}(\mathbf{v}\times\mathbf{H})\,.\,\mathbf{ds}\\&=-\frac{1}{c}(\mathbf{ds}\times\mathbf{v})\,.\,\mathbf{H}\end{aligned}$$

(since the product of three vectors $(\mathbf{a}\times\mathbf{b})\,.\,\mathbf{c}$ is the volume of the parallelepiped **abc**, and is therefore a symmetrical function of the three vectors).

But $\mathbf{ds}\times\mathbf{v}$ is the area of the parallelogram whose sides are **ds** and the distance moved by the field in one second;

$(\mathbf{ds}\times\mathbf{v})\,.\,\mathbf{H}$ is therefore the magnetic flux crossing $\mathbf{ds}$ per second. Inventing a symbol $\dot{\Phi}_{ds}$ for this quantity, which does *not* mean the rate of increase of any actual quantity Φ, we have

$$\mathbf{E}\,.\,\mathbf{ds}=-\dot{\Phi}_{ds}/c.$$

Hence for a complete circuit or path, p, the e.m.f is

$$\oint_p \mathbf{E}\,.\,\mathbf{ds}=-\dot{\Phi}_p/c, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\dot{\Phi}_p$ means the flux actually crossing the line p per second. This result is obviously perfectly general in spite of the restrictions we have made in the proof.

Precisely similar reasoning, starting from (5), gives for the magnetomotive force round a path p, due to the relative motion of the path of an electric field,

$$\oint_p \mathbf{H}\,.\,\mathbf{ds}=\dot{\Psi}_p/c, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $\dot{\Psi}_p$ is the electric flux crossing p per second.

The equations (4), (5), (6), and (7) must be regarded as universally true (although the relative velocity of path and field is often impossible to determine independently of these relations) whether or not there are charges, currents, etc., in the field. It is only when we come to deal with the *surface* integrals $\Phi=\int\mathbf{H}\,.\,\mathbf{dS}$ and $\Psi=\int\mathbf{E}\,.\,\mathbf{dS}$ taken over surfaces bounded by p, or rather with their rates of change, that the equations must be modified.

For free space, however, **E** and **H** being solenoidal, the rate at which flux (magnetic or electric) crosses the boundary p is always equal to the rate of increase of the flux over any surface bounded by p, or of "the flux through p." We thus have the two circuital relations for free space leading, by Stokes's theorem, to Maxwell's electrodynamic equations for free space

$$\oint \mathbf{E}\,.\,\mathbf{ds}=\frac{1}{c}\frac{d\Phi}{dt}=\frac{1}{c}\frac{d}{dt}\int\mathbf{H}\,.\,\mathbf{dS}\,. \quad . \quad . \quad . \quad (8)$$

and

$$\oint \mathbf{H}\,.\,\mathbf{ds}=-\frac{1}{c}\frac{d\Psi}{dt}=-\frac{1}{c}\frac{d}{dt}\int\mathbf{E}\,.\,\mathbf{dS}. \quad . \quad . \quad (9)$$

Moreover, since there is no such thing (microscopically speaking) as a free pole, (8) is true universally.

With regard to (9), however, the case is different, since if there are charges in the field, even stationary ones, we cannot properly speak of *the* electric flux through p at all, the flux over different surfaces bounded by p being different. If there are moving charges, the flux over any one surface changes discontinuously by the amount $-4\pi e$ every time a charge e crosses that surface in the positive direction. While, therefore, (7) remains true, (9) must be modified to take account of moving charges or of currents, if we wish to express the relation by a surface integral. This modification is made by adding to the surface-integral of $\mathbf{E}$ the quantity $4\pi e$ every time a charge e crosses our surface of integration S. This neutralizes the change of flux $-4\pi e$, which has no relation either to the motion of flux across the boundary p or, consequently, to the magnetomotive force, but depends on the position of the surface S, which is quite arbitrary, except as to its boundary.

This can be expressed in symbols if we suppose electric charge to cross S continuously by elements de in time dt, for we then have

$$\int \mathbf{H} \, . \, \mathbf{ds} = \frac{1}{c}\left(\frac{d}{dt}\int \mathbf{E} \, . \, \mathbf{dS} + 4\pi \frac{de}{dt}\right),$$

or for a continuous current-distribution

$$\oint \mathbf{H} \, . \, \mathbf{ds} = \frac{1}{c}\int (\dot{\mathbf{E}} + 4\pi \mathbf{j}) \, . \, \mathbf{dS},$$

where $\mathbf{j}$ is the current density, which includes, of course, the true dielectric displacement current but no "æther displacement current."

If there is no macroscopic change of flux, but only "continuous currents," we have $\dot{\mathbf{E}} = 0$, and

$$\oint \mathbf{H} \, . \, \mathbf{ds} = 4\pi i/c,$$

where i is the current through p.

So much for the two circuital relations leading to the electrodynamic equations. As to the other two equations of the field, the electrostatic equation, div. $\mathbf{E} = 4\pi\rho$, and the magnetostatic, div. $\mathbf{H} = 0$, the ordinary proof of the former fits into the present scheme, but the latter is more consistently proved thus:—

The magnetic intensity due to a moving charge may be written, by (2),

$$\mathbf{H} = -\frac{1}{c} e \mathbf{v} \times \nabla \frac{1}{r}.$$

Operating by ∇. gives

$$\operatorname{div} \mathbf{H}=0.$$

It should be noted that there are assumptions in this argument which imply immediate action at a distance, and are therefore true only for quasi-stationary fields. These assumptions are : (1) the inverse square law for poles and charges, and (2) Newton's third law. It is remarkable, however, that the relations deduced from these assumptions turn out to be universally true when they are relations between quantities existing together in space and time.

In this scheme the ordinary relations between *currents* and magnetic fields are, of course, to be deduced by summing the forces on the moving electrons in an element of wire.

The Electrical Laboratory,
Oxford,
14th May, 1926.

XCVII. *Observations concerning the Artificial Disintegration of Elements.* *By* J. Chadwick, *Ph.D., Fellow of Gonville and Caius College, Cambridge*[*].

§ 1. THE first observation of the artificial disintegration of an element was made by Sir E. Rutherford[†] in 1919, when he found that the passage of swift α-particles through nitrogen was accompanied by the appearance of particles of long range, which he supposed were hydrogen nuclei, or protons, ejected from the nitrogen nucleus by a close collision with an α-particle.

Later, Sir E. Rutherford and the writer[‡] re-examined this effect in nitrogen, and, with the improved methods of counting scintillations then available, it was found that the protons arising from the disintegration of nitrogen by collision with α-particles from radium C had a maximum range in air of 40 cm. Since the maximum range of the swift protons obtained when these α-particles are passed through hydrogen is about 30 cm., this observation showed definitely that no unforeseen contamination with hydrogen could be responsible for the results, and opened the way to the examination of other elements. The element under test was bombarded by the α-particles from a source of radium active deposit, and a search was made for H-particles of more than 32 cm. range, that is, beyond the range of any particles due to hydrogen, whether free or in combination, in the material under examination. In this way we found unmistakable evidence of the disintegration of six elements: boron, nitrogen, fluorine, sodium, aluminium, and phosphorus. Many other elements were examined, but no certain evidence of disintegration resulting in the expulsion of protons of long range was found. Attempts were made to prepare materials free from hydrogen and to pursue the examination at absorptions less than 30 cm. of air. The results obtained in these experiments were, however, too indefinite to allow any conclusions to be drawn. It was found that some protons are always present under these conditions, whatever the material under examination, some are emitted from the source itself, and some are due to hydrogen contamination of substances in the path of the α-particles. The examination at small absorptions is further complicated by the presence of long-range α-particles from the source of radium C, which are emitted in such numbers as probably to mask completely the small effect to be expected from disintegration of the bombarded material.

---

[*] Communicated by the Author.

[†] Rutherford, Phil. Mag. xxxvii. p. 538 (1919).

[‡] Rutherford and Chadwick, Phil. Mag. xlii. p. 809 (1921).

These experiments had, however, shown that the protons liberated in disintegration were emitted in all directions. We * therefore proceeded to search for particles ejected from the bombarded material in a direction at right angles to the direction of the incident α-particles. This method has the advantage that hydrogen in the material no longer affects the results, and also that the number of long-range α-particles scattered at 90° is so small as to be negligible. The examination can thus be pursued with safety down to an absorption corresponding to 7 cm. of air, and with special precautions to still smaller absorptions in the case of the lighter elements. In this way we found evidence of the disintegration of all elements from boron to potassium inclusive, with the two exceptions of carbon and oxygen. We could detect no effect which could be ascribed with certainty to the disintegration of carbon or oxygen. The elements immediately beyond potassium gave somewhat indefinite results. In most cases we observed the liberation of a small number of H-particles, but these appeared to be due to the presence of nitrogen in the materials examined. For example, a piece of Swedish iron gave, on the first

---

* Rutherford and Chadwick, Nature, cxiii. p. 457 (1924); Proc. Phys. Soc. (London), xxxvi. p. 417 (1924).

examination, a small but quite definite number of H-particles. After the iron had been heated in a vacuum for some hours, this effect was reduced to a small fraction of its first value. The effect was therefore attributed to the presence of some active element, probably nitrogen. Similar results were obtained with the other elements in this region between potassium and iron. Experiments with heavier atoms showed that any disintegration effect, if present at all, was very small indeed.

The experiments of Sir E. Rutherford and the writer have shown, then, that all light elements up to and including potassium can be disintegrated by collision with an α-particle of 7 cm. range, with the exceptions of helium, lithium, beryllium, carbon, and oxygen. With these, and with the heavier atoms, we have been able to detect no certain evidence of disintegration as manifested by the expulsion of hydrogen nuclei.

On the other hand, Kirsch and Pettersson * have recently published accounts of experiments which lead to very different conclusions. These workers have observed, under similar conditions to those holding in our experiments, the disintegration not only of those lighter elements such as carbon and oxygen for which we failed to obtain any evidence of disintegration, but of almost every element they have been able to examine. For example, Kirsch and Pettersson find that when carbon, whether as graphite, diamond, or carbon dioxide, is bombarded by α-particles the emission of protons can always be detected. The number of protons obtained from carbon is for very small absorptions about the same as the number they observe from aluminium, but the ranges are much shorter, the maximum range being about 16 cm. in the direction of the incident α-particle, and about 8 cm. at right angles to this direction. These particles should have been recorded in the experiments of Sir E. Rutherford and myself, and it is a very surprising fact that we have been unable to detect them. Our failure to do so is attributed by Kirsch and Pettersson to the low numerical aperture of the microscopes we use for observing scintillations. This explanation, which I shall consider later, is advanced by these authors as the general reason why our observations give no evidence of disintegration in so many cases where they have obtained positive results.

It must be pointed out here that, even in the few cases where both our observations and those of the Vienna workers

---

* Kirsch and Pettersson, *Wien. Ber.* 1923 and later years. 'Atomzertrümmerung' (Leipzig, 1916).

agree in showing a disintegration effect, the agreement is more apparent than real. We may take as examples the cases of magnesium and silicon. For both these elements Kirsch and Pettersson find a disintegration effect several times greater than we observe, while the maximum ranges of the particles are actually much smaller than we measure. On the supposition that we cannot observe weak scintillations it is to be expected that we should find smaller maximum ranges than Kirsch and Pettersson.

Many more such discrepancies between the Vienna observations and ours might be quoted, but sufficient has been said to show that differences exist of a very serious character. In this paper I shall discuss various points connected with experiments on the artificial disintegration of elements by collision with α-particles, and I shall endeavour to show that we have good reason for holding to the results obtained in this laboratory.

§ 2. *The Optical Systems used in Counting.*

I have mentioned already that Kirsch and Pettersson have suggested, in order to explain the discrepancies between our experiments and theirs, that our optical system is so weak in light-gathering power that we cannot observe the weak scintillations produced by H-particles of low range. Before discussing the question of the minimum energy of the H-particle which can be detected under our conditions of experiment, a few details of our optical arrangement will be given.

It is evident that the first and essential property of a scintillation microscope must be that its light-gathering power should be sufficiently high to enable the observer to count the scintillations with ease and certainty. The second demand to be satisfied is that the field of view should be so large that the scintillations under observation are received in convenient numbers for counting. Further, the magnification of the system should not be less than about 30 ×, for experience shows that with low magnifications some counters fail to observe a fairly large fraction of the scintillations.

In the work in which we are interested here, we have to record chiefly the scintillations due to H-particles of varying ranges. The scintillations are, on the whole, not so bright as those due to an α-particle of a few centimetres range, and those due to H-particles near the end of their range are very weak indeed. The microscope must therefore have a high numerical aperture. On the other hand, the disintegration of a nucleus by collision with an α-particle is a very rare event, and the number of H-particles received on the screen is usually small, of the order of 1 per minute per sq. mm. of screen. For many reasons it is unsatisfactory to deal with fewer than 20 scintillations per minute, that is, to work with a field of view of less than 10 sq. mm. area. The scintillation microscope must therefore possess not only a high numerical aperture but also a large field of view, two mutually opposed qualities. We have found that the Watson Holoscopic objective of 16 mm. focal length and ·45 numerical aperture satisfies these two conditions sufficiently well for general purposes. The numerical aperture is high enough to enable H-particles of short range to be counted, and a very large field of view can be obtained when a suitable eyepiece is used. For example, an ordinary eyepiece, such as the Watson Holoscopic, gives with this objective a field of view of about 8 sq. mm. area, while a specially constructed wide-angle eyepiece gives a field of 50 sq. mm. The magnification of the latter system is about 35×. We have used this combination for some years and found it quite satisfactory for general use. The scintillations produced by H-particles of short range are very weak, but they can be counted without undue strain and with consistent results. If a higher numerical aperture is desirable, the Watson Holoscopic objective of 12 mm. focal length and ·65 numerical aperture may be used. The scintillations then appear brighter, but the same field of view cannot be obtained.

At the same time we did not ignore the possibility that the above optical arrangement might not be sufficiently powerful to detect very weak scintillations. While it appeared unlikely that one could fail to observe the scintillations due to H-particles of more than a few centimetres range, there was always the possibility that other products of disintegration might be present which might give scintillations too weak to be observed with this system. In order to test this point a special microscope * was constructed for me about two years ago by Adam Hilger and Co. The eyepiece is very similar to that used in the system described above, but the objective is designed solely for the observation of scintillations. A detailed description of this objective will be published later by Mr. Perry, of Adam Hilger and Co., who is responsible for its calculation and design, but a brief account of its main

---

* The cost of this microscope was covered by a grant from the Caird Fund, for which I am indebted to the Council of the British Association.

features may be given here. In order to keep the numerical aperture as high as possible the first surface of the objective is also the scintillation screen, that is, the zinc sulphide is deposited on the surface of the objective itself. This front surface is hemispherical and about 106 sq. mm. of the surface can be obtained in good focus. The area of the projection of the object-field on a plane perpendicular to the axis of the microscope is about 80 sq. mm. In the correction for extra-axial foci, coma is eliminated, but residual astigmatism remains, the resulting image of a point being sharply focussed as an astigmatic line. This appeared to be the best type of correction possible for the purpose in view, since it is essential to secure the greatest concentration of light in the image. A scintillation which occurs near the edge of the object-field is thus seen as a narrow line of light, whilst those in the centre appear as usual as bright points. The numerical aperture of this objective is 1·06, and the magnification of the system of objective and eye-piece is × 32.

In this microscope there are thus combined a very high numerical aperture and a large field of view, with good definition and a sufficient magnification. It seems unlikely that any considerable improvement could be made in this system. The numerical aperture might perhaps be increased slightly, but only by the sacrifice of a large part of the field of view.

With this special microscope the scintillations, both those of α-particles and those of H-particles, appear much brighter. The improvement is particularly marked in the case of the weak scintillations produced by H-particles of short range. Comparative tests in which this microscope and the old one were used under the same experimental conditions showed however, that while the counting was much easier with the new microscope about the same number of scintillations was observed with both. We found no evidence that scintillations could be observed with the Hilger microscope which were not visible with our old system. We concluded, therefore, that in general our observations of scintillations were trustworthy and that we were not failing to record the existence of particles owing to any weakness in our optical arrangement.

§ 3. *The Efficiencies of Counters.*

A further question arises, however, as to our personal powers of observing scintillations. We have had a long and varied experience in counting scintillations, and our assistants have been carefully trained. Comparison of the observations of one counter with those of another has revealed only small variations in efficiency, and we have no evidence that one counter can observe scintillations of a type which are invisible to another. The actual efficiency of an observer can be determined by a method due to Geiger and Werner*, which was used by them, in their measurement of the number of α-particles emitted by radium, to eliminate errors of counting caused by fatigue or lack of concentration. The method consists in the simultaneous observation of the scintillations on the same screen by two counters. The zinc-sulphide screen can be observed through each of two microscopes. The area of the screen covered by zinc sulphide is so small that all the crystals are visible through each microscope. Each observer records the occurrence of a scintillation through an electrical contact key on the tape of a chronograph. Now every scintillation which occurs on the screen should be visible to both observers, and, if both are perfect counters, should be recorded at the same time by each, and all the marks recorded by one observer A should coincide with those of the second, B. It is found, however, that all the marks do not coincide; some scintillations are seen by A which are not recorded by B, and *vice versa*. From the tape record of a large number of observations we can deduce both the actual number of scintillations which occurred and the efficiencies of the counters. If N is the number of scintillations which actually occurred on the screen and λ_1 is the probability that the counter A sees and records a scintillation, *i. e.* his efficiency in counting, then on the average he will make $N_1=\lambda_1 N$ marks on his tape. Similarly counter B will record $N_2=\lambda_2 N$ scintillations, where λ_2 is B's efficiency. The number of coincidences on the tape, or the number of scintillations which both A and B see, will be $C=\lambda_1\lambda_2 N$. The record on the tape gives N_1, N_2, and C at once, and thus N, the number of scintillations which actually occurred, and λ_1, λ_2, the efficiencies of the two counters, can be calculated.

This method of testing the efficiency of counters has been used in this laboratory during the past two years. The microscopes used in these tests consisted of the Watson Holoscope objective of ·45 n.a. and a low-power eyepiece. The field of view had an area of nearly 8 sq. mm. About thirty students have been examined, the majority of whom had had no previous experience of counting. When the scintillations are produced by α-particles of a few centimetres

---

[*] Geiger and Werner, *Zeit. f. Phys.* xxi. p. 187 (1924).

range, even an untrained observer will count about 80 per cent. of the scintillations, and his efficiency generally rises in a short time to about 95 per cent. With scintillations due to α-particles of not more than a few millimetres range, the untrained observer may count only 60 to 70 per cent. at first, but in the course of time his efficiency will again rise to more than 90 per cent.

A series of experiments has also been carried out on the counting of scintillations due to H-particles. Three observers were used, A and B having had considerable experience in counting, having counted in many of the disintegration experiments, while C was relatively untrained. The source of H-particles was an α-ray tube containing radium emanation. The outer surface of the tube was coated with a layer of paraffin wax of 25 μ thickness and a sheet of aluminium foil of about 5 cm. stopping power. The H-particles falling on the screen had a maximum range of about 7 cm. in air. As no magnetic field was used to deflect the β-rays emitted by the emanation tube away from the ZnS screen, the screen was much brighter than one would use under normal conditions. In spite of this, the results of the test showed that A counted about 88 per cent,, B about 80, and C, the untrained observer, about 60 per cent. of the scintillations.

The conditions in these experiments were much less favourable to accurate counting than in any of our observations of the disintegration particles. These tests therefore give good grounds for the belief that the counting in the disintegration experiments was trustworthy, and that no large fraction of the scintillations present on the screen had been missed *.

§ 4. *The Detection of H Particles of Short Range.*

As far as our experience goes there is, on the average, little difference in the efficiencies of our counters. Occasionally it has been observed that a counter, owing to ill-health or some other temporary cause, has recorded in one experiment consistently fewer particles than the others ; but even in such a case the difference has been small. Taking the whole of our counting observations into consideration, we must conclude that one counter can see what is visible to another. This may mean either that particles even of very short range produce a scintillation which can be seen by most observers, or that the limit of vision is about the same for most observers. This question is connected with that of the intensity of the scintillation which can just be detected under the conditions prevailing in our experiments, or rather of the energy of the α-particle or of the H-particle which gives rise to such a scintillation. We already possess a certain amount of information on this point. For example, in the experiments of Bieler and the writer[*] on the collisions of α-particles with H atoms, scintillations produced by H-particles of about 2·5 cm. range were counted consistently and without difficulty. Again, Sir E. Rutherford[†] has observed scintillations due to α-particles the velocity of which was only ·15 of that of the α-particle of radium C. This velocity corresponds to an energy of only 2 per cent. of that of the radium C α-particle, or to a range of ·24 mm. [A proton of the same energy would have a range of about ·7 mm.] In both these cases the optical system consisted of a Watson objective of ·45 n.a. and a low-power eyepiece, that is, very similar to that used in many of the disintegration experiments. It seems clear, then, that in these latter experiments we should certainly have been able to detect any H-particles of range greater than 3 cm. in air. To make the matter more conclusive, however, a special series of experiments was carried out to test whether, under as far as possible the same conditions as in the disintegration experiments, H-particles of still shorter range could be observed. The H-particles of definite maximum range were produced by the impact of α-particles on H atoms, in paraffin wax in some cases, and in hydrogen gas in others. If the range of a H-particle projected in the direction of the colliding α-particle is R_0, then the range of the H-particle projected at an angle θ to this direction will be $R=R_0\cos^3\theta$. Now both scintillation and ionization measurements agree in giving a value of about 30 cm. of air for R_0, when the range of the colliding α-particle is 7 cm. If we take $\theta=45^\circ$ we get $R=10{\cdot}6$ cm. Even if the error in R_0 should be as great as 3 cm., the error in R will be only 1 cm. If we use a beam of α-particles of shorter range than 7 cm., the range of the H-particles produced by it will be correspondingly reduced. In this way it is possible to obtain a beam of H-particles the maximum range of which is known with sufficient accuracy. By placing absorbing screens of mica in the path of this beam we can adjust the maximum range of the H-particles to any desired smaller value. The beams of H-particles defined in this way were received on a zinc-sulphide screen and observed under similar conditions to those prevailing in the disintegration experiments. The experimental arrangement is shown in fig. 1.

---

* One point of interest may be mentioned here in connexion with these experiments. When the scintillations appear on the screen at convenient intervals, it is possible for the two observers to compare their impressions of the intensity of the scintillation. It sometimes happens, particularly when dealing with the weaker scintillations, that a scintillation which appears bright to one observer is weak to the other.

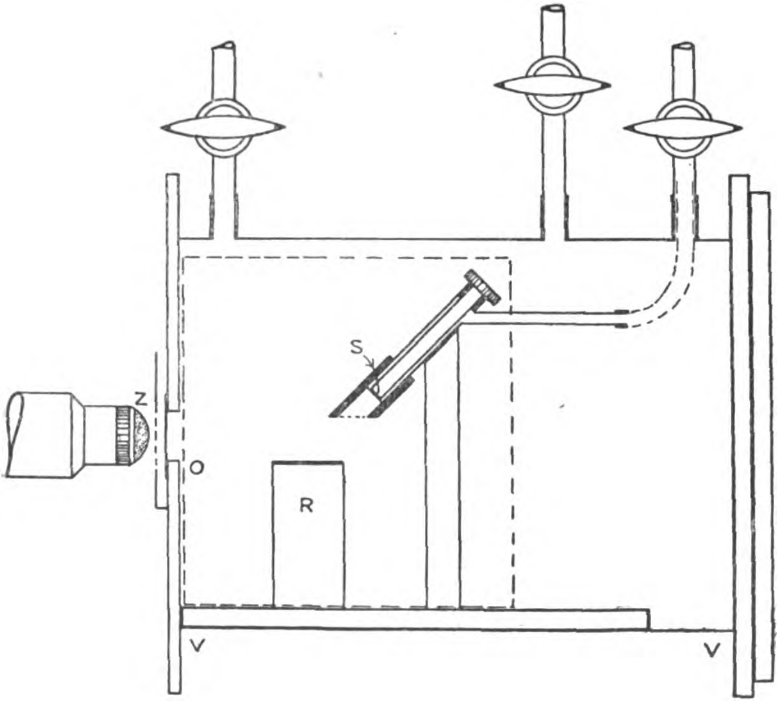
---

[*] Chadwick and Bieler, Phil. Mag. xlii. p. 923 (1921).

[†] Rutherford, Phil. Mag. xlvii. p. 277 (1924).

The source of α-rays was placed at S in a brass tube with a graphite extension which served to limit the beam of α-rays to a suitably narrow cone. The H-particles were produced in a film of paraffin wax placed on the graphite support R. This support and the source-holder were carried on a slide fitting into the brass box VV. This box could be evacuated. The H-particles produced in the film of paraffin wax were observed on the zinc-sulphide screen Z. The window O in the face of the box, through which the H-particles passed, was covered with a sheet of mica equivalent in stopping power to 2·6 cm. of air. Further

Fig. 1.



absorbing screens of mica could be inserted between this window and the ZnS screen. A magnetic field was applied to deflect the β-rays emitted by the source away from the ZnS screen.

The source of α-rays was a brass disk of 3 mm. diameter coated with radium active deposit. In order to obtain a beam of H-particles of suitable range, the source was covered with a sheet of mica of 3·35 cm. stopping power. The α-particles incident on the paraffin wax thus had a maximum range of 3·65 cm. The H-particles were observed in a direction at 45° to the direction of the incident α-particles. The maximum range of the H-particles projected in this direction was therefore 5·5 cm. Owing, however, to the finite widths of the cone of α-rays and of the cone of H-particles received on the screen, there were a few particles present with greater ranges, up to 8·3 cm. When the total absorption in the path of the H-particles was 4·3 cm. of air, that is, most of the particles had ranges less than 1·2 cm. while a few still had 4 cm. range, the number of scintillations was comparatively large. When the absorption was increased to 7·0 cm., some scintillations were still observed. That these were due to H-particles from the paraffin wax was shown by replacing the film by a thin sheet of graphite, when no scintillations were observed beyond those due to the natural effect of the screen.

In other experiments the paraffin wax was removed and the box VV was filled with hydrogen at atmospheric pressure. Similar results were obtained, in that scintillations were observed when the maximum range of the H-particles falling on the screen was not more than 6 mm.

Some experiments have been carried out with an apparatus of similar type to that used in the work of Bieler and the writer. In these the H-particles were observed at angles between 60° and 70° to the direction of the incident α-particles. The results again showed that the scintillations produced by H-particles of ranges less than 1 cm. can be counted consistently.

In these experiments both the Watson objective of ·45 n.a. and the special Hilger microscope were used. While the greater numerical aperture of the Hilger microscope rendered the counting of these weak scintillations much easier, there was no evidence that with this microscope scintillations were visible which could not be seen with the other. Since in the above experiments H-particles of only a few mms. range were observed consistently by all our counters, it would seem that the energy necessary to produce a visible scintillation must be extremely small. In other words, the retina of the dark-adapted eye must be able to detect exceedingly small amounts of light. It is possible to form an estimate of the amount of light received by the retina in the observation of a scintillation. For this purpose we may take the observation of Sir E. Rutherford that α-particles of radium C possessing only ·15 of their initial velocity still produce a visible scintillation. The energy of such an α-particle is $2{\cdot}75 \times 10^{-7}$ erg. Now Marsden * has shown that the visible light of the scintillation contains about 1·5 per cent. of the energy of the α-particle. Hence the energy of the total amount of light emitted in the scintillation observed by Rutherford was about 4×10^{-9} erg. The objective through which the scintillation was viewed had a numerical aperture of ·45, and therefore collected about one-twentieth of the total light emitted by the scintillation. The energy finally received on the retina, omitting losses due to reflexion and absorption, was thus about 2×10^{-10} erg.

This result is in general agreement with observations on the sensitivity of the dark-adapted eye made by many workers, in particular by Grijns and Noyons †, and by du Noüy ‡. A close comparison with the results of these observers is not possible since the scintillation observations are made under rather different conditions. It may be mentioned, however, that Noyons was able to detect under suitable conditions an amount of white light of about 4×10^{-11} erg. Since the eye is relatively insensitive to light of the longer wave-lengths, Henri and des Bancels § have concluded that the dark-adapted retina can just detect an amount of green light of energy about 5×10^{-12} erg, roughly one quantum. The visual spectrum of the light emitted in a scintillation in zinc sulphide has its maximum in the green at about 515 $\mu\mu$, very close to the region of wave-lengths to which the eye is most sensitive. It seems very probable, then, that we should be able to detect by their scintillations α-particles of even smaller energy than those observed by Rutherford. If we assume that the H-particle is as efficient in producing a scintillation as the α-particle, it appears that we should be able to observe the scintillations due to H-particles of ranges of only a few tenths of a mm. of air.

---

* Marsden, Proc. Roy. Soc. A, lxxxiii. p. 548 (1910).

† Grijns and Noyons, *Müller's Arch. f. Phys.* p. 25 (1905).

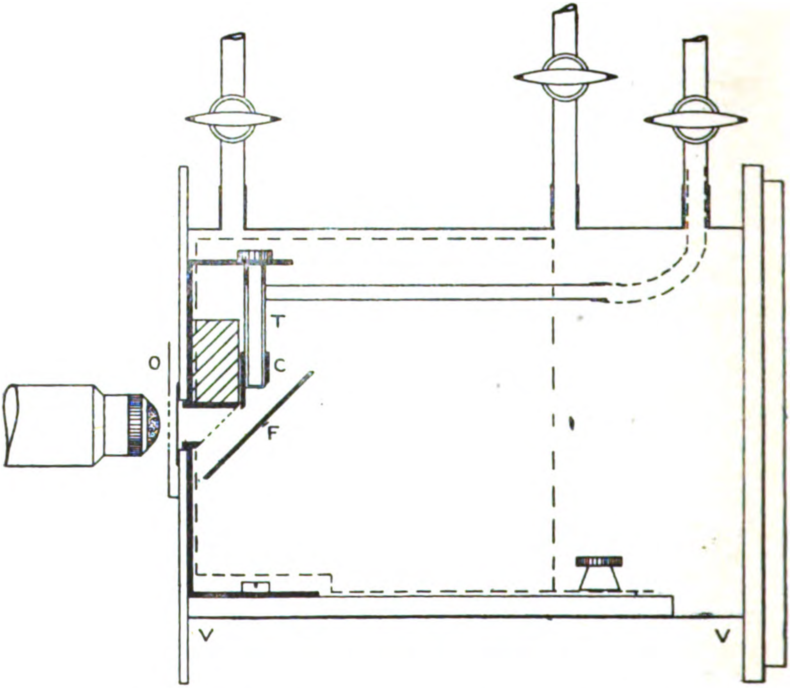
‡ du Noüy, J. Gen. Phys. iii. p. 743 (1920).

§ Henri and des Bancels, *J. Phys. Path. Gen.* xiii. p. 841 (1911).

§5. *Experiments on the Disintegration of some Light Elements.*

The experiments described in the last two sections show that our observation of scintillations is reasonably efficient, and that the optical systems used in the disintegration experiments are sufficiently powerful to enable us to detect the presence of H-particles of short ranges. It seems then that the differences between our results and those of Kirsch and Pettersson cannot be explained by their suggestion that our optical arrangement is too weak. Before discussing these differences in further detail I shall now give an account of some recent experiments in which the effects were observed when certain light elements were bombarded by α-particles.

Fig. 2.



The experimental arrangement will be clear from the diagram of fig. 2, and need not be described in great detail.

The source, a small disk coated with radium active deposit, was enclosed in a brass tube T, which could be evacuated independently of the box VV. The end of the tube T was covered with a thin sheet of collodion of 2 to 3 mm. air equivalent. A diaphragm C of graphite served to limit the beam of α-particles. The material to be bombarded was placed at F, and was carried on a graphite frame. This was placed in position on slides fixed to two graphite plates (shown by dotted lines). Observations were made at an angle of 90° to the beam of α-particles. The window O in the face of the box was covered with a sheet of mica of 2·6 cm. air equivalent. The zinc sulphide screen, in these experiments the front surface of the Hilger microscope, was brought opposite this window at a distance of about 3 mm. Absorbing screens of mica or aluminium could be introduced between the window O and the ZnS screen. The box was placed between the poles of a magnet in order to reduce the luminosity of the screen caused by scattered β-rays.

As usual in experiments of this kind, precautions were taken against extraneous effects due to scattered α-particles and to contamination. To avoid the presence of scattered α-particles all surfaces exposed to the source were covered with sheets of graphite, except of course the material under examination. Owing to the low atomic weight of carbon, the α-particles scattered at an angle of 90° have a range only ·354 of the incident range. The α-particles in these experiments had a range of about 6·8 cm. after passing through the fixed collodion film. The range of the α-particles scattered from the graphite walls at an angle of 90° was therefore 2·4 cm. Such α-particles were completely absorbed in the mica window at O and failed to reach the ZnS screen. Owing to the width of the beam of α-particles it was possible for α-particles to reach the window which had been scattered through only 75°. It was therefore not possible to eliminate completely the extraneous effects below an absorption of about 3·5 cm.

The disturbing effect of contamination was guarded against by enclosing the source in the tube T, and in addition by passing a slow stream of oxygen through the box. The oxygen was led in through a series of fine holes in the face of the box. The pressure of oxygen in the box was between 1 and 2 mm. of mercury. With these precautions contamination was only occasionally observed. Any experiment in which it occurred was rejected.

The results observed in these experiments may be summarized very briefly. When an aluminium foil of 2·6 cm. air equivalent was bombarded, the number of H-particles observed at ranges greater than 8 cm. of air was nearly 4 per minute per mgm. activity of the source. When the box was filled with dry air to atmospheric pressure and no radiator was used, *i. e.* nitrogen was under bombardment, about 4 to 5 particles per minute per mgm. were observed at an absorption corresponding to 6 cm. of air. These experiments gave a standard with which to compare the results obtained with the other elements to be specially examined, viz., lithium, beryllium, carbon, and oxygen.

A piece of metallic beryllium of a high degree of purity was used. The total absorption in the path of the H-particles was equivalent to 3 cm. of air. An average of ten scintillations per minute was observed, giving nine after deduction of the natural effect of the screen. The activity of the source was 43 mgm. When an extra absorbing screen of 1·3 cm. of air was inserted in the path of the particles, the number of scintillations fell to the natural effect. On replacing the beryllium radiator by a dummy carbon frame, we observed at an absorption of 3 cm. seven scintillations (net) per minute, the source having then decayed to 32 mgm. The effect observed at an absorption of 3 cm. was thus the same when the beryllium radiator was away as when it was present, and it has been pointed out above that a few scattered α-particles might be expected at this absorption. We concluded that the few scintillations observed were due to α-particles scattered at smaller angles than 90° by the carbon surfaces, and that there was no residue to be ascribed to the beryllium. There were no particles present with ranges greater than 4 cm. of air.

Similar results were found with carbon and oxygen. A sheet of Acheson graphite served as a carbon radiator, while for oxygen the box was filled with the gas to atmospheric pressure. In both cases there was no evidence of the emission of H-particles with ranges greater than 4 cm. of air.

The experiments with lithium as radiator were not so definite. At the smallest absorption scintillations were observed to the number of about 1 per min. per mgm. The number decreased rapidly as the absorption was increased, and fell to the natural effect of the screen at a total absorption of 4·3 cm. The scintillations appeared rather bright for H-particles of such short range, and it seems probable that they were due to α-particles scattered by a small sodium impurity in the specimen of lithium. This explanation is supported by the observed range of the particles and by the fact that different samples of lithium gave different numbers of particles under the same conditions of experiment. We can, however, say definitely that no particles were observed which had ranges greater than 4·3 cm. of air.

Those observations confirm the earlier experiments of Sir E. Rutherford and the author in showing no evidence that the nuclei of lithium, beryllium, carbon, and oxygen are disintegrated by collision with an α-particle. The number of H-particles with ranges of more than 4 cm. in air liberated from these elements is certainly less than one-fortieth of the number ejected from aluminium under the same conditions. Pettersson *, on the other hand, found for both beryllium and carbon a relatively large number of H-particles at low absorptions. At an absorption of 4 cm. there were present roughly as many H-particles as we observe from an aluminium radiator, while the maximum ranges of the H-particles observed at 90° to the incident α-particles was about 8 cm. in the case of carbon, about 9 cm. for beryllium. The tests described in the previous sections have shown that our counters are able to observe consistently the scintillations due to H-particles of only a few mms. range. It seems most unlikely that they should all fail to observe those due to H-particles of 4 cm. range, and we are forced to the conclusion that no such particles are present in our experiments.

In the same series of experiments, Pettersson observed the disintegration of silicon. The number of H-particles was roughly the same as for beryllium or carbon, and the maximum range of the particles was only slightly greater, about 10 or 11 cm. of air. Silicon behaves, therefore, according to these results, in a very similar way to carbon and beryllium. One would expect that, if our failure to observe the particles from carbon and beryllium is due to inefficiency of counting, we should fail also to observe the particles from silicon. This, however, is not the case. As we have stated previously, Sir E. Rutherford and the writer have also found that silicon is disintegrated by α-particles. We observed relatively far fewer H-particles than Pettersson, but found that the maximum range was much greater, about 24 cm. of air. Though the agreement between the two sets of observations is more apparent than real, yet the comparison of the results strengthens the conviction that our counting is efficient.

The objection may be raised that the experiments described above offer no evidence as to whether the elements beryllium, carbon, etc., disintegrate with the emission of H-particles of

---

* Pettersson, *Wien. Ber.* cxxxiii. p. 445 (1924).

very short range. The difficulty in observing such α-particles lies in the presence of the scattered α-particles. While an α-particle of moderate range, say about 2 cm., produces a much brighter scintillation than does a H-particle of the same range, it is difficult in practice to distinguish the scintillations seen on the screen as due to α or to H particles. The beam of scattered α-particles contains α-rays of all ranges up to the maximum scattered range, and those of short range predominate, for although the beam of incident α-particles is homogeneous, the radiator is usually infinitely thick, considered from the point of view of α-ray scattering. The scintillations produced by such a scattered beam will be mainly very weak, with relatively few bright ones. To distinguish separately the scintillations produced by a small number of H-particles superposed on this scattered beam, is, as far as our experience goes, impossible to achieve. We have found it advisable to restrict the investigations for products of disintegration to the region beyond the range of the α-particles scattered from the elements under examination.

The Vienna workers, on the other hand, claim to be able to distinguish the scintillation produced by a H-particle from that due to a scattered α-particle, and, relying on this, they have pursued the search for H-particles to the smallest absorptions, well within the range of the scattered α-particles. This difference in procedure is partly responsible for the difference between their results and ours. To take one example out of many, we may discuss the observations on the disintegration of aluminium.

§ 6. *Comparison of Observations on Aluminium.*

Schmidt[*], working in Vienna, found no evidence of a lower limit to the ranges of the H-particles liberated from aluminium, and indeed the majority of the H-particles he observed had ranges less than 4 cm. of air. He also compared the effects when aluminium was bombarded by α-particles of different ranges, and found that H-particles were still liberated when the impinging beam of α-rays had only 1·3 cm. range. The number of H-particles liberated from a thin sheet of aluminium by α-rays of low speed was not smaller than the number found when high speed α-rays were used, but the ranges of the H-particles were shorter.

These results are very different from those obtained in this laboratory, where we have observed that the H-particles liberated from aluminium have a minimum range of about 10 to 12 cm. of air, and that α-rays of short range are unable to disintegrate the aluminium nucleus. In our early experiments we observed few, if any, H-particles of range greater than 30 cm. when aluminium was bombarded by α-particles of less than 4·9 cm. range, but did not pursue the examination to smaller absorptions. I have recently re-examined the effect of bombarding aluminium by α-particles of different ranges, using the apparatus shown in fig. 2. The H-particles were therefore observed at right angles to the direction of the beam of incident α-particles, and the observations could be carried down to the range of the scattered α-particles. It was found that as the range of the incident α-particles was reduced, the number of H-particles observed, and also their maximum range, decreased until with α-particles of about 3 cm. range no definite evidence of H-particles could be detected *. The H-particles liberated by α-particles of short range still showed a minimum range of about the same value as observed for those ejected by fast α-particles.

---

[*] Schmidt, *Wien. Ber.* cxxxiv. (1925). This paper was not available to me. His results are taken from Kirsch and Pettersson, 'Atomzertrümmerung.'

In earlier papers † it has been assumed that the force exerted by the nucleus on a positive charge changes in the nucleus or very close to it, from a repulsive force varying as the inverse square of the distance to one of attraction of more rapid variation. On this view there must be a critical surface around the nucleus at which the force is zero or the potential a maximum. The H-particle emitted from the nucleus in disintegration cannot escape from the nucleus with less final energy than corresponds to the potential at this critical surface. The H-particles must thus have a certain minimum range corresponding to this potential. However the disintegration of the nucleus is brought about, whether by swift α-particles or those of energy just sufficient to produce disintegration, the liberated H-particles cannot have less than this range. Further, no α-particle will cause disintegration unless it has sufficient energy to penetrate within this critical surface. We are thus able from the observations to obtain approximate values for the potential of this surface, both from measurements of the minimum ranges of the liberated H-particles and from the range of the

---

* It is difficult to fix this minimum range of the effective α-particle with any accuracy. The beams of α-rays of short range are obtained by placing absorbing screens of mica over the source of radium B+C, and since a wide cone of rays must be used in order to obtain a measurable effect the beam is necessarily heterogeneous.

† Rutherford and Chadwick, *loc. cit.*

α-particle which is just able to produce disintegration ; and from this we can make an estimate of the distance of the critical surface from the centre of the nucleus, or of the "size" of the nucleus.

Whatever view one may take of the structure of the nucleus or of the laws of force inside it, one would expect the H-particle emitted in disintegration to possess a minimum range corresponding to the energy gained in its flight down the electrical field of the nucleus, and also corresponding to the energy of the α-particle which is just able to bring about disintegration. Since we know that the law of force is at least approximately that of the inverse square except at very close distances, we can again make some estimate of the "size" of the nucleus.

Interpreting our observations in this way, we find that the aluminium nucleus has a radius of about 8×10^{-13} cm.

The experiments of Schmidt would make the aluminium nucleus much larger, of radius about 20×10^{-13} cm. Indeed, his observation that many of the liberated H-particles have ranges corresponding to less than 1 cm. of air would make the nucleus even larger than this.

It seems to me improbable that the nucleus of aluminium can be so large, for the experiments of Sir E. Rutherford and the writer on the scattering of α-particles have shown that aluminium behaves normally when the distance of collision between the nucleus and the α-particle is about 10 to 12×10^{-13} cm.; the scattering by the silver nucleus, which one would expect to be larger than the aluminium nucleus, is normal for collisions at a distance of 20×10^{-13} cm. These scattering experiments therefore support in a general way our observations on the disintegration of aluminium. It may be objected that Schmidt's observations have been carried further than ours, in that we have made no attempt to search for H-particles of range less than about 3 to 4 cm. of air. On the general views outlined above, one must expect that the H-particle must acquire in falling down the electrical field of the nucleus an energy sufficient to give it a range nearly three times the range of the α-particle which is just effective in producing disintegration. For example, an α-particle of 3 cm. range, if just able to disintegrate the aluminium nucleus, should liberate H-particles with a minimum range of nearly 9 cm. To observe these it is not necessary to pursue the observations within the range of the scattered α-particles.

In my opinion, the difference between our results and those of Schmidt is chiefly due to his procedure in counting within the range of the scattered α-particles, and in judging from the brightness of the scintillation whether it was due to an α-particle or to a H-particle. As I have stated previously, we have never, in this laboratory, felt confident of our ability to pick out the scintillations of H-particles from those of a heterogeneous beam of α-particles, although we have had considerable experience in counting.

§ 7. *Summary.*

In this paper I have pointed out the conflicting nature of the results in investigations of the disintegration of elements by collisions with α-particles obtained by workers in Vienna and by Sir E. Rutherford and myself. While the former workers find that disintegration with the liberation of H-particles seems to be a common property of all elements, we find that only the lighter elements can be disintegrated and among these there are certain striking exceptions.

Our failure to observe the effects found in Vienna has been attributed by Kirsch and Pettersson to the unsatisfactory optical equipment at our disposal for the counting of scintillations. I have endeavoured to show here that this explanation is without foundation and that we can in fact observe with our microscopes the scintillations produced by any H-particles which are likely to be emitted in the disintegration of a nucleus. Our optical systems have been described, and the results of some tests of the efficiencies of our counters have been given, together with some observations of scintillations due to H-particles of short range.

Experiments have been made to re-examine the elements lithium, beryllium, carbon, and oxygen, but no evidence of disintegration has been detected. These results confirm the previous experiments carried out in this laboratory, but are in sharp disagreement with those of the Vienna workers.

I am unable to suggest any explanation which will account satisfactorily for the differences between these results and those obtained in Vienna. In certain cases it seems possible that their procedure of picking out the scintillations due to α-particles and those due to H-particles by the difference in brightness has led to error. Some of the conflicting results in the investigations of aluminium may perhaps be explained in this way. The main points at issue however, still remain without explanation.

Cavendish Laboratory,
Cambridge.

XCVIII. *Scattering of Positive Rays by Gases.—II.* By G. P. Thomson, *M.A.*, *Fellow of Corpus Christi College, Cambridge, and Professor of Natural Philosophy in the University of Aberdeen* *.

THE experiments described in this paper are a continuation of those recently published in this magazine † on the scattering of positive rays in hydrogen. The gases investigated are helium and argon, with a few experiments on oxygen. With a few minor modifications, mentioned below, the apparatus is the same as that described in the previous paper, to which reference should be made for details. The following is an outline of the method. A beam of positive rays was obtained by making a fine slit in the cathode of a discharge-tube, and fitting a similar parallel slit some distance behind. This heterogeneous beam then passed between the plates of a condenser, and thus was deflected into an energy spectrum. A small portion of the deflected rays was sorted out by means of a diaphragm with a slit ·5 mm. wide, which allowed rays to pass of a certain small range of energy, the average of which could be adjusted at will by changing the potential difference, maintained between the plates of the condenser by a battery of dry cells. The rays thus isolated passed through the scattering chamber (10 cm. long) and struck a photographic plate which could be raised and lowered as required. In the absence of scattering, the developed plate would have shown an approximately uniform blackened strip about 1·8 mm. wide, being the projection by the rays of the ·5-mm. slit on the plate. Actually this strip was always bordered by a fainter blackening, due to the rays whose paths had been deflected from a straight line by collisions with the molecules of the gas. The intensities of the scattered rays at various distances from the edge of the main beam were measured photometrically. For the method used to calibrate the plates, and other photographic details, see the previous paper.

Experiments in Argon and Helium.

There was one important difference between these experiments and the previous ones. Previously the rays (protons) were derived from the gas (hydrogen) used for the scattering. In this case it was desired to test the scattering of protons

---

* Communicated by the Author.

† Phil. Mag. vol. i. p. 961 (1926).

by the inert gases, and it seemed probable at first that different gases would have to be introduced into the discharge-tube to form the rays, and the scattering chamber to scatter them. It was found, however, that the persistence of hydrogen in the positive rays is so great that even after several hours' running, with a stream of argon or helium passing through the apparatus, the hydrogen rays were still far the strongest, as shown by a test exposure which was taken on each plate, with the addition of a magnetic field to form a mass spectrum. No doubt this is partly due to the much greater sensitivity of the photographic plate to the fast hydrogen rays, and probably, if an electrical method of measuring the rays had been used, the result would have been very different. Nevertheless it is remarkable that, in some 60 photographs taken, the helium or argon lines were only visible, and that very faintly, on two or three, in spite of the fact that the spectrum of the discharge showed only helium or argon, as the case might be, and H_β. By far the strongest line on the mass spectrum was the H_+, or proton; the H_{2+} was very faint with helium, and, though rather stronger in argon, was under 15 per cent. of the strength of H_+ except in one or two plates, which were rejected for that reason. In addition, many of the plates showed a faint line at a mass of about 14, though with the very small dispersion available it could not be measured accurately. This is probably due to the layer of air formed on the glass and metal when the apparatus is opened to the atmosphere to change a plate. The traces of air in the spectrum of the discharge were, however, very slight, and it is unlikely that the impurity was sufficient to affect the results to the order of accuracy of the experiment.

The helium used was given me by Sir J. J. Thomson. It was purified before use by fractionation over charcoal in liquid air.

I am indebted for the argon to the Research Department of the General Electric Company. It was 98 per cent. pure, the impurity being nitrogen and oxygen. It was further purified before use by being passed several times over calcium turnings at a bright red heat.

Results.

As in the case of hydrogen, each experiment gives a curve showing the relation between the density of the scattered radiation at any point and the distance of the point from the edge of the main beam. This curve can be used to calculate the collision relation between a ray and a molecule of the gas. The experiments were made with rays of various velocities and with various pressures in the scattering chamber. It was found that the shape of the curves was the same in both the gases, and was independent of the velocity within the errors of experiment. Thus the intensity at any fixed point of the curve can be taken as a measure of the scattering in investigating the way in which it depends on the speed of the rays.

Variation with Pressure.

In the case of helium it was found that consistent results were obtained by supposing that the scattering was proportional to the pressure, provided that the criterion for "single" scattering (see the previous paper) was satisfied. The results for argon, however, showed great discrepancies, if it was assumed that the scattering was proportional to the pressure as indicated by a McLeod gauge connected with the scattering chamber. The explanation is as follows. For helium, as for hydrogen, a tube filled with charcoal and immersed in liquid air was in close connexion with the scattering chamber through a tap of wide bore. In the argon experiments it was feared that this would lead to too great an absorption of argon, and that the gas left in the scattering chamber would be largely the residual hydrogen from the discharge. Thus the charcoal was turned off, or only used in CO_2 snow. The effect of this was that the vapour from the taps, some of which (such as the one which served as a winch to lower the plate) were unavoidable, was present in the scattering chamber and produced an effect equivalent to about ·003 mm. of argon. A similar effect has also been observed by Rückhart [*]. In consequence of this it was necessary to make observations at a number of pressures, and draw the graph, a straight line, in order to determine the scattering due to the argon itself. A specimen graph is shown in fig. 1. The work thus became very laborious, as, in general, only one photograph can be taken in a day, and some of these have to be rejected owing to changes in the discharge, shown either by changes in the observed pressure or by differences between the blackness of the check exposures at the beginning and end of the series.

Variation of Scattering with Speed of Rays.

However, fig. 2 shows the scattering for helium and argon plotted against the velocity of the protons. The scattering is measured in arbitrary units and at an arbitrary pressure 4/1000 mm., the same for each gas. The most interesting point about the result is that they show a *maximum* of scattering at certain speeds. It is surprising

---

[*] *Ann. Physik,* lxxiii. p. 73 (1923).

Fig. 1.

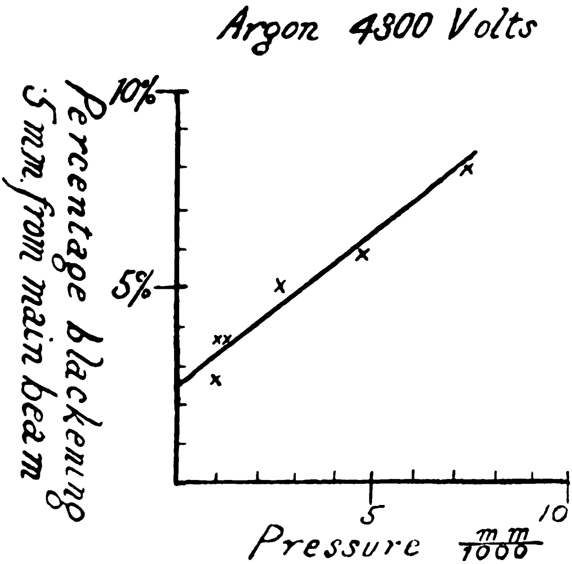
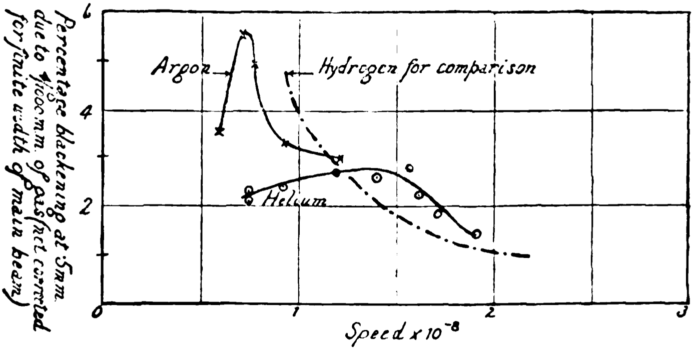


Fig. 2.



that the scattering should ever decrease with decreasing speed of the rays, but it will be remembered that Ramsauer and others have found an analogous effect in studying the absorption of slow electrons by gases. They observed that the absorption was a maximum for a certain speed, and decreased for smaller speeds. It is of importance that these speeds are of the same order as those found in the present experiments, though of course the energies were much less, owing to the smaller mass of the electrons. Thus with argon Ramsauer found a maximum at $2{\cdot}1\times10^8$ against $\cdot75\times10^8$ in the present experiment, and with helium one at $1{\cdot}35\times10^8$ against $1{\cdot}4\times10^8$. Further, in both experiments the maximum for argon is a sharp one and that for helium flat.

Collision Relation.

It is theoretically possible to calculate, from a knowledge of the density of the scattered radiation at various distances from the main beam, the chance that a ray shall be deviated through a given angle by a collision with a gas molecule. If there are N molecules per c.c. in the gas, we may write the chance of a collision as $N\psi(\theta)\,d\theta\,dx$ for a deviation between θ and $\theta+d\theta$ in the element of path dx. In the actual experiment the deflexions occur throughout the whole length of the scattering chamber, and are equally in all directions, while only the components perpendicular to the plane of the beam are observed. This has the effect of, as it were, blurring the features of the function ψ, so that its precise form cannot be determined with certainty. However, the general rate of change of number scattered with angle can be determined with some accuracy, so that if it is assumed that $\psi(\theta)$ is a power of θ, say $A\theta^{-n}$, the values of n and A can be found. This seems to be the best way of expressing the results of the experiments; but it must be emphasised that the form assumed for ψ is arbitrary, and probably almost any functional form which gave the same average rate of variation over the range of angles considered would fit the experiments almost as well. Once, however, a power law is assumed, n can be found with tolerable accuracy. The following is an outline of the method by which A and n can be determined.

For collisions occurring in a small element dx of the path of a ray, the chance of a collision between θ and $\theta+d\theta$ is $AN\theta^{-n}\,d\theta dx$. The surface density of the scattered particles on unit sphere with centre at dx is proportional to $AN/2\pi\theta^{n+1}$. In these experiments it is only scattering perpendicular to the slit which matters, and if ϕ is the projection of θ in this direction (see fig. 3), the chance of a scattered ray lying between ϕ and $\phi+d\phi$ is

$$\frac{d\phi}{\pi}\int_0^{\frac{\pi}{2}}\frac{AN\phi\sec^2\alpha\,d\alpha}{\phi^{n+1}\sec^{n+1}\alpha}=\frac{d\phi}{\phi^n}\cdot\frac{AN}{2\sqrt{\pi}}\cdot\frac{\Gamma(n/2)}{\Gamma(n/2+1/2)}=B\phi^{-n}\,d\phi,\ \text{say.}$$

The rays may be regarded as diverging from the centre of the condenser, and scattering may occur before or after the limiting diaphragm is reached. The pressure was such that the chances of multiple scattering can be neglected, and the scattering is considered as equally likely to occur at all points of the path of the ray. It is obvious that the law as stated can only hold if θ exceeds a certain minimum, otherwise the chance of scattering is no longer small. In practice this is allowed for by only measuring the scattering some little distance from the edge of the main beam. (For a discussion of the conditions to be observed so that the combined effect of a number of small deflexions is negligible, see the previous paper.)

Fig. 3.

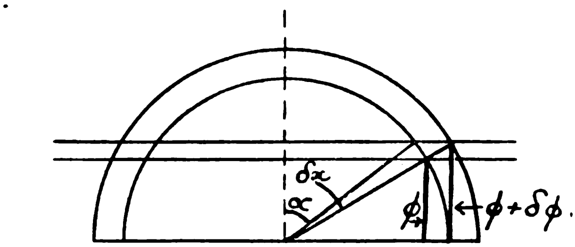
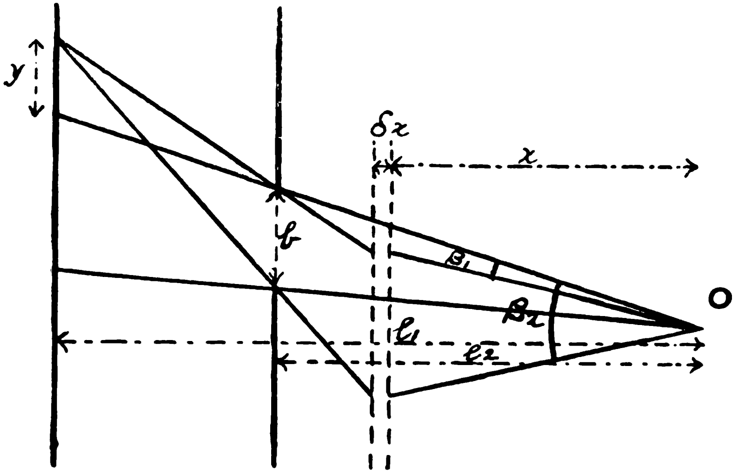


Fig. 4.



Let M$d\beta$ be the number of rays starting from O in the angle between β and $\beta + d\beta$ (see fig. 4). The value of ϕ for a ray to be scattered from a point (x, β) to a point on the plate at a distance y from the edge of the main beam is $\phi=\frac{y+\beta l_1}{l_1-x}$, the angles all being small.

The density at y due to scattering from $x\,d\beta\,dx$ will be

$$\mathrm{BM}(l_1-x)^{n-1}(y+\beta l_1)^{-n}\,dx\,d\beta.$$

The limits for β when $0<x<l_2$ are β_1 and β_2 namely

$$y(l_2-x)/x(l_1-l_2) \quad\text{and}\quad \{y(l_2-x)+b(l_1-x)\}/x(l_1-l_2).$$

When $l_2<x<l_1$, the limits for β are 0 to b/l_2. A straightforward integration gives for the total effect

$$\frac{\mathrm{BM}(l_1-l_2)^{n-1}}{n(n-1)}\left\{\frac{1}{y^{n-1}}-\frac{1}{(y+2a)^{n-1}}\right\},$$

where $2a=bl_1/l_2$, the width of the main beam at the plate. The density at y as a fraction of that of the main beam is thus

$$\frac{\mathrm{AN}}{2\sqrt{\pi}}\cdot\frac{\Gamma(n/2)}{\Gamma(n/2+1/2)}\cdot\frac{l_1(l_1-l_2)^{n-1}}{n\,.\,(n-1)}\left\{\frac{1}{y^{n-1}}-\frac{1}{(y+2a)^{n-1}}\right\}^{*}.$$

From the observed variation of density with y, the best value of n was determined by trial and error, and A can then be found.

For both argon and helium, $n=1{\cdot}35$ was found to give the best fit at all speeds. Values of A are shown in the table. Fig. 2 shows the scattering at an arbitrary point

Table of Values of $\mathrm{A}\times10^{18}$ *for Various Gases.*

Velocity.		Argon.	Helium.	Hydrogen ($n=2$).
$\cdot 6\times10^{-5}$	....	6·5		
·7	....	10·2	4·0	
·8	....	6·9	4·3	
·9	....	6·3	4·5	1·75
1·0	....	5·9	4·8	1·40
1·2	....	5·6	5·1	1·05
1·4	....	...	5·2	·76
1·6	....	...	4·5	·56
1·8	....	...	3·2	·47
2·0	....	...	...	·36

---

* *Correction.*—For the inverse square law of force $n=3$, and we have $\frac{\mathrm{AN}}{24}\,l_1(l_1-l_2)^2\left\{\frac{1}{y^2}-\frac{1}{(y+2a)^2}\right\}$. On pp. 973-4 of the previous paper, the factor $(l_1^3-l_2^3)$ is given instead of $l_1(l_1-l_2)^2$ in calculating the scattering to be expected on the inverse square law. The calculated figures on p. 974 are thus in error. As, however, the effect is to accentuate the differences between the observed and calculated values, the conclusion (that the inverse square law is inadequate) is not affected.

near the middle of the region studied, so as to make a rough comparison possible with hydrogen, for which n is different (approximately 2·0).

Oxygen.

Experiments had previously been made with oxygen. In this case it was necessary to have a stream of hydrogen flowing through the discharge-tube, and one of oxygen through the camera. Some mixing, of course, occurred through the slits in the cathode. This was allowed for approximately by measurements of the pressure when each stream was flowing separately, but the method is not very accurate. The amount of scattering, also, was too large for the scattering to be entirely "single." It could not be sufficiently reduced, as the amount of hydrogen present was fixed by the requirements of the discharge, and enough oxygen had to be present in the camera for its pressure to be comparable with that of the oxygen there. These difficulties might have been overcome by re-designing the apparatus, but it was felt that the preliminary results did not show sufficient points of interest to justify the expenditure of time, and that the inert gases were a more promising field. It was found, however, that the scattering per molecule in oxygen was much more than (about five times) that in hydrogen. The scattering seemed to increase with decreasing velocity throughout the range studied. The form of the collision relation was much the same as for the inert gases.

Discussion.

The most important point which emerges from these experiments is the analogy between scattering of protons and absorption of electrons shown by the occurrence of maxima at *velocities* of the same order (in the case of helium the velocities are the same within the experimental error). The natural explanation is some form of resonance effect, and it is important that the speeds are of the same order as those of the electrons in the outer Bohr orbits. The positive ray results are, however, much harder to explain on ordinary mechanics, because it is difficult to see how an electron moving in an orbit can produce much effect on a particle 1850 times its mass and moving with about the same speed. The angles of scattering observed are of the order ·015, and from the conservation of momentum they can only occur if the atom moves as a whole to an appreciable extent. If the nucleus and electrons in the atom act separately on the ray according to the Coulomb law, or indeed any law of the same general kind, the speed, or indeed the existence, of an electron can only matter if it is sufficiently firmly attached to the nucleus to be able to transfer a considerable amount of momentum to it.

The forces required to transfer this momentum are much larger than are usually supposed to be exerted on outer electrons. The inner electrons in argon would be expected to produce an appreciable effect; but their speeds are much greater than those of the rays, and so it is difficult to see how they can account for the maximum. It looks as though the atom must be regarded as a whole for the purposes of collisions of this kind, the periods associated with it being concerned with the whole mass and not merely with a particular electron. Alternatively one could suppose that the electrons are held rigidly in their orbits by some unknown forces. Dempster [*] has found that protons of about 900 volts pass through hydrogen and helium without becoming neutralized, and apparently without appreciable scattering. The method of experiment used by me is limited on the side of small velocities by the inefficient blackening produced. Indeed, I should probably not have been able to go so far as I did in the case of argon but for a batch of plates which was appreciably more sensitive to slow rays than those used for hydrogen.

It is hoped to continue the experiments on hydrogen, by another method, for slower speeds in order to see if there is a maximum in this case also.

My sincere thanks are due to the Department of Scientific Research for a grant towards the expenses of an assistant, Mr. J. D. McKay, to whose able help I am much indebted.

Summary.

The experiments are in continuation of those described in Phil. Mag. (May 1926). It is found that argon and helium show a maximum of scattering for a certain velocity of proton ($\cdot 75 \times 10^8$ and $1\cdot 4 \times 10^8$ respectively). This result appears to be analogous to those of Ramsauer and other workers with electrons of about the same speed, but is still more difficult to reconcile with the ordinary mechanical models of the atoms concerned. The experiments are consistent with a collision relation of the form $A\theta^{-1\cdot 35}$ in the case of both helium and argon, the index being independent of the speed. A few experiments on oxygen show large scattering but apparently no maximum.

Aberdeen, Sept. 1926.

---

[*] Nat. Acad. Sci. vol. xii. p. 96 (1926); Nat. Acad. Sci. vol. xi. p. 552 (1925).

XCIX. *The Activity Coefficients of Aqueous Hydrochloric Acid at Extreme Dilutions.* *By* GORDON NONHEBEL, *B.A., B.Sc., Assistant Lecturer in Chemistry at the University of Leeds* *.

THE present values of the activity coefficients of hydrochloric acid in aqueous solutions are based on the E.M.F. measurements of Linhart † and on the freezing-point measurements of Randall and Vanselow ‡. In both cases an extrapolation of the experimental points to infinite dilution is necessary for the calculation of the activity coefficients, and for this reason some uncertainty still exists as to their true values. Owing to experimental difficulties, the data of Randall and Vanselow are somewhat irregular in the most dilute solutions, while the data of Linhart are not sufficiently numerous to admit of an unchallenged extrapolation.

Linhart measured the E.M.F. of cells H_2/HCl, aq./AgCl : Ag at 25° C.; if M is the molality of the acid and γ the activity coefficient, then the observed electromotive force is given by $E = E_0 - 2\frac{RT}{F}\ln M\gamma$. E_0 is a constant which is determined by extrapolation of the quantity $E_0' \left(= E + 2\frac{RT}{F}\ln M\right)$ to infinite dilution, at which γ is, by definition, equal to unity. Linhart himself gave $E_0 = 0{\cdot}2234$ volt, but his extrapolation was probably faulty, as he plotted E_0' against the logarithm of the concentration. Randall and Vanselow, by combining the activity coefficients calculated from their cryoscopic measurements with the E.M.F. data of Linhart in more concentrated solutions, found $E_0 = 0{\cdot}2230$; and by a plot of Linhart's values for E_0' against the square root of the concentration found $E_0 = 0{\cdot}2231$.

Debye's expression for the interionic forces in an aqueous solution of a uni-univalent electrolyte § leads to the limiting equation

$$-\log\gamma = 0{\cdot}5\ M^{\frac{1}{2}} \text{ at } 25^\circ.$$

Since

$$E_0' = E + 0{\cdot}1183 \log M = E_0 - 0{\cdot}1183 \log \gamma,$$

it follows that at extreme dilution E_0' should vary as $0{\cdot}05915\ M^{\frac{1}{2}}$. By making the curve $E_0'/M^{\frac{1}{2}}$ tangential to a line of this slope 0·05915, Scatchard found $E_0 = 0·2226$ volt [*], a method of extrapolation which is open to criticism. In a later paper [†] he has suggested that the value of E_0 might be lowered to 0·2224 in order to better the agreement between the experimental data and the complete Hückel equation [‡], in which account is also taken of the variation of the dielectric constant of the solution with the concentration. By plotting values of E_0 calculated from Milner's equation, of E_0 calculated from Debye's limiting equation, and of E_0' against the square root of the concentration, and by extrapolating the three curves to the same point, Nonhebel and Hartley [§] concluded that the most probable value of E_0 was $0·2229 \pm 0·0001$ volt.

---

* Communicated by Dr. J. W. Nicholson, F.R.S.

† Journ. Amer. Chem. Soc. xli. pp. 1175 (1919).

‡ *Loc. cit.* xlvi. p. 2418 (1924).

§ *Physikal. Z.* xxv. p. 97 (1924).

In the work to be described, an attempt has been made to establish the value of E_0 for cells H_2/HCl, aq./$AgCl : Ag$ at 25° by the determination of sufficient experimental points to place the slope of the E_0' curve beyond doubt. Once E_0 is accurately known, reliable values for the activity coefficients may readily be calculated from the experimental data.

EXPERIMENTAL.

In view of the extreme dilution of the solutions, it is obvious that the slightest trace of impurity in the water may alter entirely their composition and properties. Uncertainty is also caused by possible adsorption of the acid on the electrodes, and by the necessity for a correction for the dissolved silver chloride, since in ten-thousandth molal solution this correction is as great as 0·6 millivolt.

Linhart used the precipitated form of silver chloride electrode. This attains equilibrium after a period which may be as long as three days, during which time the solution may easily become contaminated. Since calomel electrodes are completely unreliable in solutions of hydrochloric acid more dilute than 0·1 M, it was decided to use the electrolytic form of silver-chloride electrode which has been shown by Scatchard and by Nonhebel and Hartley (*loc. cit.*) to be reproducible to 0·1 mv. Such electrodes come to equilibrium rapidly, but will not maintain a constant potential in very dilute acid solutions for more than 36 hours.

In order to avoid contamination of the solutions by exposure to the atmosphere, a weighed amount of conductivity water was placed in the cell, and known quantities of a more concentrated solution of the acid added from a weight pipette. By making further additions when the cell had come to equilibrium, several concentrations could be studied with the same electrodes. The electrode vessel consisted of a "well-aged" Jena flask of 250 c.c. capacity, stoppered with a five-holed rubber bung. This carried the iridized gold hydrogen electrode, two silver-chloride electrodes, and a tube with a fine jet for the inlet of the hydrogen. A central tube, carrying the outlet bubbler on a ground over-cap, was used for the insertion of the weight pipette. The bubbler for saturating the incoming hydrogen with water-vapour was attached to the cell by means of a ground-joint, and was filled with conductivity water. The tubes carrying the electrodes etc. were of borosilicate glass. The rubber bungs were freed from uncombined sulphur by boiling in caustic-soda solution, washing with dilute acid and then with conductivity water.

---

[*] Journ. Amer. Chem. Soc. xlvii. p. 641 (1925).

[†] *Loc. cit.* xlvii. p. 2098 (1925).

[‡] *Physikal. Z.* xxvi. p. 93 (1925).

[§] Phil. Mag. (6), l. p. 729 (1925).

The hydrogen and silver-chloride electrodes were freshly made for each run; they were prepared in the manner described by Nonhebel and Hartley for methyl-alcohol solutions, except that the silver-chloride electrodes were chloridized by electrolysis in an aqueous N/10 solution of the acid. After preparation, they were soaked in conductivity water for four hours before insertion in the cell. The hydrogen was generated by electrolysis of baryta; it was freed from spray by passage through a U tube packed with cellulose, and from traces of oxygen by passage over a hot tungsten filament. The freedom of the hydrogen from spray was proved by passing it through conductivity water for some time. The water used in these experiments had a conductivity of 0·5 reciprocal megohm; it was freed from dissolved air by evacuation in order to prevent the formation of air-bubbles on the electrodes and walls of the flask when the cell was placed in the thermostat. The solution of hydrochloric acid added from the weight pipette was approximately 0 07 N, and was standardized, through baryta, against constant boiling hydrochloric acid by weight titration. Owing to condensation of water in the tube leading to the exit bubbler, the concentration of the solution in the cell could not be known with an accuracy much greater than 0·2 per cent., corresponding with an error in E_0' of less than 0·1 mv.

The electrical apparatus was the same as that used by Nonhebel and Hartley. All the measurements were carried out at 25° ± 0·01°.

Experimental Procedure.—The Jena flask was dried and filled with a weighed amount of evacuated conductivity water. The electrodes, which were prepared the same day, were then mounted in the stopper, dried by touching their edges with filter paper, and inserted in the cell. Usually the cell was placed in the thermostat and the water saturated with hydrogen overnight; additions of acid were then commenced the following morning. The cells came to equilibrium within three hours of the first addition, but on further additions, equilibrium was reached within half an hour. A measurement was not accepted until the E.M.F. was constant for at least one hour. It was not found possible to make more than four additions in each run, as the electrodes then became sluggish and the silver-chloride electrodes often began to show discrepancies among themselves. An attempt was made to reach solutions of concentrations less than 0·0001 M, but experiments showed that at these dilutions the electrodes failed to come to equilibrium.

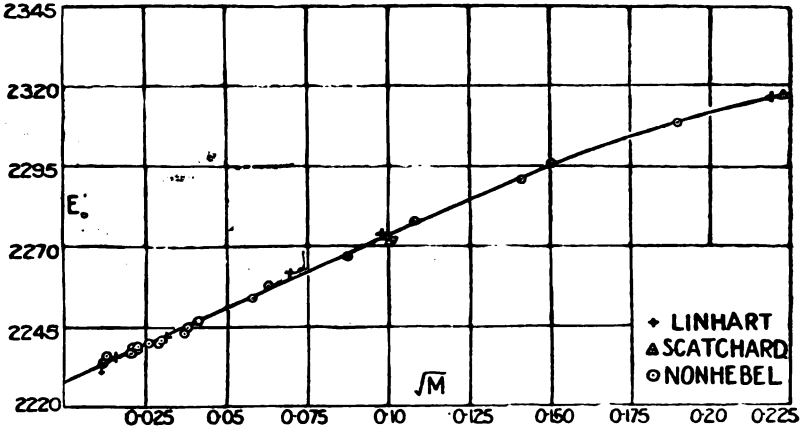
RESULTS.

All the observed E.M.F.'s have been corrected to a partial pressure of hydrogen of 760 mm. For the most dilute solutions correction also has been made for the solubility of the silver chloride in the manner described by Linhart. These corrected results, together with those obtained by Linhart and by Scatchard, are given in Table I. in order

TABLE I.

Series.	M.	E.	E_0'.
VI, i	0·0001182	0·6897	(0·2250)
Linhart	·0001360	·6805	·2231
II, i	·0001529	·6748	·2234
IV, i	·0001602	·6726	·2236
Linhart	·0002420	·6514	·2236
II, ii	·0004185	·6233	·2237
I, i	·0004381	·6210	·2237
V, i	·0004579	·6189	·2239
Linhart	·0004830	·6161	·2238
IV, ii	·0005060	·6137	·2238
VI, ii	·0005071	·6137	·2239
I, ii	·0006793	·5987	·2240
III, i	·0008540	·5870	·2240
V, ii	·0008915	·5849	·2241
Linhart	·001000	·5791	·2242
I, iii	·001376	·5628	·2243
VII, i	·001467	·5597	·2245
II, iii	0·001705	0·5522	0·2247
IV, iii	·001850	·5480	·2247
II, iv	·003377	·5178	·2254
III, ii	·004006	·5094	·2258
Linhart	·004826	·5002	·2262
VII, ii	·007687	·4768	·2267
Linhart	·009650	·4658	·2274
Scatchard ...	·01002	·4638	·2273
,, ..	·01010	·4633	·2272
,, ...	·01031	·4623	·2272
III, iii	·01166	·4565	·2278
III, iv	·01970	·4309	·2291
VII, iii	·02263	·4242	·2296
VII, iv	·03616	·4015	·2309
Linhart	·04826	·3874	·2317
Scatchard ...	·04986	·3858	·2318

of ascending concentration, but the series in which the measurement was made is shown in the first column. Concentrations are expressed in gm. equivalents per 1000 gm. water. The figure shows a plot of E_0' against the square root of the molality: within the experimental error this curve is a straight line up to at least 0·005 M, and the points lie less well on the curve suggested by Scatchard*. The value of E_0 is therefore best calculated from the experimental data by the method of least squares, assuming that the equation to the curve is $E_0' = E_0 + \sigma \sqrt{M}$. If this equation is true, then the activity coefficients are given by $-\log \gamma = A \sqrt{M}$, where the coefficient A is equal to $\sigma/0{\cdot}1183$. Values of E_0 and of A calculated in this manner from the experimental data are given in Table II.



E_0' for cells H_2 | HCl aq | AgCl : Ag

TABLE II.

Concn. range to zero ...	0·001	0·002	0·005	0·012 M
E_0 (volts)	$0{\cdot}2228_6$	$0{\cdot}2228_7$	$0{\cdot}2227_6$	$0{\cdot}2228_0$
A	$0{\cdot}35_1$	$0{\cdot}35_8$	$0{\cdot}39_6$	$0{\cdot}38_2$

It was deemed inadvisable to weight any of the points, though the first two in a run were possibly the more reliable. The most probable value of E_0 appears to be 0·2228 ± 0·0001 volt, in fair agreement with the value 0·2226 volt obtained by Scatchard by extrapolation of

---

* Journ. Amer. Chem. Soc. xlvii. p. 641 (1925).

Linhart's data. It is to be noted, however, that in his extrapolation Scatchard has made the line concave to the concentration axis in order to accommodate the point obtained by Linhart at the highest dilution measured, namely 0·000136 M. This does not seem to be justifiable in view of Linhart's belief that the point was unreliable and probably too low in value.

The most probable value of A is 0·39. According to the theory of Debye, $-\log\gamma = 0{\cdot}505\sqrt{M} - BM$, but up to 0·001 M the term BM may be neglected without appreciable error. Milner's calculation, on the other hand, leads to the equation $-\log\gamma = 0{\cdot}37\sqrt{M}$ approximately *, which agrees fairly well with the value 0·39 obtained experimentally. It seems evident, therefore, that for aqueous hydrochloric acid, as for its solutions in methyl alcohol †, the theory of Debye, while predicting correctly the general shape of the activity-concentration curve, gives too great a value for the slope A ‡.

SUMMARY.

The E.M.F. of cells H_2/HCl aq./AgCl : Ag have been measured over a range of concentration extending from 0·00015 M to 0·04 M.

A new method of procedure for the measurement of these cells has been described.

The results indicate that the activity coefficient-concentration curve up to 0·005 M is given by the equation $-\log\gamma = A\sqrt{M}$, in which the constant A is equal to 0·39, a value somewhat smaller than that demanded by the equation of Debye for the interionic attraction in a strong electrolyte.

The author's thanks are due to Mr. D. M. Murray-Rust for carrying out two of the runs independently, to the Department of Scientific and Industrial Research for a maintenance grant, and to General H. B. Hartley, F.R.S., for valuable advice and encouragement during the progress of the investigation. The experimental part of this work was done at the Balliol and Trinity College Laboratory, Oxford.

August 1926

---

* See Nonhebel and Hartley, *loc. cit.*

† See, however, Scatchard, Phil. Mag. (7), ii. p. 577 (1926).

‡ In this connexion, see Pike and Nonhebel, Phil. Mag. l. p. 723 (1925).

C. *On the Oblique Rebound of a Ball from a Fixed Plane.*

By R. C. J. Howland, *M.A.*, *M.Sc.*, *University College, London*, *and* T. W. Dickson, *B.A.*, *City and Guilds (Engineering) College, London* *.

Summary.

A ball was dropped on to a fixed inclined plane, describing a trajectory after rebound. From direct observation of the path the nature of the rebound was deduced. As a result the usually accepted law of rebound is shown to be false, and an alternative law is suggested.

Introductory.

The usually accepted laws of rebound may be summarized as follows :—

(1) The relative velocity normal to the surfaces at their point of instantaneous contact is reversed in direction and reduced in a ratio e. This ratio, generally called the coefficient of restitution, is a constant for the bodies concerned.

(2) The tangential impulse will be just sufficient to destroy the relative tangential velocity of the points in instantaneous contact unless the impulse required for this exceeds a certain limit.

(3) This limit is reached when the ratio of the tangential impulse to the normal impulse is equal to the coefficient of statical friction between the surfaces.

(4) When the tangential impulse needed to annul the relative tangential velocity exceeds this limit, the relative velocity is no longer destroyed : the ratio of the impulses remains at its limiting value.

For a ball striking a fixed plane, it is a consequence of these laws that the tangents of the angles of incidence and reflexion are proportional to one another for values of the angles below certain critical values, and are linearly related for larger values of the angles. The existence of these linear relations was confirmed in a series of rather rough observations by Mr. H. G. Green †. It is evident, however, that the truth of the laws cannot be inferred from these relations.

---

* Communicated by Prof. S. Chapman, D.Sc., F.R.S.

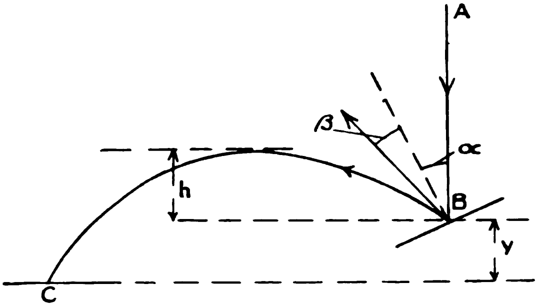
† "On a Method of Measurement of Newton's Coefficient of Restitution and the Law of Oblique Impact." Phil. Mag. l. pp. 187–194 (1925).

In some experiments undertaken for a different purpose, Mr. L. Hock observed the trajectories of balls dropped vertically and rebounding from an inclined plane [*]. The range on a horizontal plane was measured, and also, in some cases, the angle of rebound. The results are compared by Mr. Hock only with the simplified theory in which the ball is treated as a particle. This naturally leads to a large discrepancy. It was, however, noticed by the present writers that, even when the theory is properly applied, a discrepancy remains. This is particularly noticeable in the angles of rebound. The angles observed indicate that the tangential impulse on the ball is considerably *greater* than that predicted by the theory. This unexpected result suggested that more refined experiments would be of interest. They were accordingly undertaken in the following manner.

Mode of Experiment.

The ball was dropped from a height on to a fixed inclined plane and allowed to rebound freely. It fell on a board covered with white paper overlaid with carbon paper, so that the range was automatically recorded. Simultaneously, the trajectory was observed end-on with a cathetometer. It was found that a very clear sight of the ball at the top of its path could be obtained and the greatest height of the trajectory thus measured.

Fig. 1.



The ball being dropped from A (fig. 1) falls through a height H and, striking the plane at B, rebounds to C, at a depth y below B. Then writing

---

[*] "Beiträge zur Prüfung des elastichen Verhaltens von Kautschuk, Stahl und anderen Stoffen," *Zeit. f. tech. Phys.* 1925.

height of top of path above B = h,
vertical velocity before impact = V,
,, ,, after ,, = v,
horizontal velocity after ,, = u,
normal velocity towards plane before impact = N,
,, ,, away from plane after ,, = n,
tangential velocity down the plane before impact = T.
,, ,, ,, ,, after ,, = t,
,, ,, of striking point of ball immediately after contact = τ,
horizontal range = R,
initial angular velocity of ball after impact = ω,
radius of ball = r,
angle of incidence = α,
,, rebound = β,

we have, neglecting air resistance,

$$V = (2gH)^{\frac{1}{2}}, \quad v = (2gh)^{\frac{1}{2}}, \quad \ldots \ldots \quad (1)$$

$$u = \frac{R}{2y}(\sqrt{v^2 + 2gy} - v), \quad \ldots \ldots \quad (2)$$

$$N = V \cos\alpha, \quad T = V \sin\alpha, \quad \ldots \ldots \quad (3)$$

$$n = v \cos\alpha + u \sin\alpha, \quad t = u \cos\alpha - v \sin\alpha, \quad . \quad (4)$$

$$e = n/N, \quad f = t/T, \quad \ldots \ldots \quad (5)$$

$$r\omega = 5(T - t)/2, \quad \tau = r\omega - t, \quad \ldots \ldots \quad (6)$$

$$\tan\beta = t/n. \quad \ldots \ldots \quad (7)$$

The nature of the rebound can thus be fully deduced from measurements of H, h, R, y, and α.

Apparatus and Materials.

Most of the observations were made with small balls of case-hardened steel of the type used for ball-bearings. The plane, of steel or glass, was bolted to a heavy anvil whose face could be clamped at any required angle to the horizontal. Initial attempts with a plane of fairly soft steel showed that a ball of ⅜ in. diameter falling from a height of about 50 cm. indented the surface considerably. This increased the resilience of the plane, and the ranges recorded in successive trials showed a systematic increase, sometimes up to 50 per cent. above the first observed. With a $\frac{1}{4}$ in. ball this effect was still too great to allow of successful experiments This trouble was never wholly got over while a steel plane was used, but fairly satisfactory results were obtained with a plane of hardened silver-steel.

The best results were obtained with a sheet of plate glass. A $\frac{1}{4}$ in. ball, falling through about 60 cm., could be allowed to drop five or six times on the same spot before the surface of the glass was much injured. This gave ample time to align the cathetometer with the top of the path.

It was, of course, important that the ball should drop without initial spin. For this purpose, electromagnetic and pneumatic releases were tried and found unsatisfactory. Finally a mechanical release was used. This consisted of a short brass bar, pivoted at one end about a horizontal axis and held in a horizontal position by a catch. When the catch was released the bar was pulled down by a spring, the initial acceleration of the free end being greater than g. The ball, previously supported in an indentation at this end, was thus left in mid-air and fell freely without spin. The satisfactory working of this release was confirmed by the consistency of the results obtained.

All the vertical measurements were made with the cathetometer. The angle of the plane was taken with a clinometer.

Experiments were also made with a golf ball falling from a height of 7 ft. on to a heavy iron plate.

Results with $\frac{1}{4}$ in. Steel Ball on Glass Plane.

The measurements made are recorded in Table I. From these the values of N, T, n, t, e, f are found from equations (1) to (5). These are shown in Table II. In Table III. will be found the values of τ, tan α, tan β, and $(\mathrm{T}-t)/(\mathrm{N}-n)$. This last measures the ratio of the tangential to the normal impulse. It should be noted that, according to the accepted theory, τ should be zero for all small values of α.

The upper limits to the experimental errors in the measurements of Table I. may be stated as 1 mm. in each of H, h, and y; 2 mm. in R; 5′ in α. Most of the errors were certainly much less than these, especially for the larger values of α. From equations (1) to (6) may be found the maximum possible errors in e, f, and τ. These are shown, for three values of α, in Table IV.

Table I.

α.	H cm.	*h* cm.	*y* cm.	R cm.
0° 0′	60·1	49·7	—	—
4 45	60·4	49·0	13·5	29·3
9 40	61·1	46·2	27·7	60·5
14 30	61·0	41·0	27·8	83·4
19 45	61·1	33·8	27·7	101·9
24 40	61·2	25·4	27·5	113·5
29 35	61·7	15·6	27·0	119·3
34 50	61·2	7·4	27·5	110·7
39 40	61·0	1·9	27·8	95·2

Table II.

α.	N.	T.	*n*.	*t*.	*e*.	*f*.
0° 0′	—	—	—	—	0·910	—
4 45	343	28·5	313	17·6	0·912	0·62
9 40	341	58·0	311	35·4	0·913	0·62
14 30	335	86·6	306	50·7	0·915	0·59
19 45	326	117	298	68·6	0·916	0·59
24 40	315	144·5	288	92·3	0·916	0·64
29 35	302	172	277	132·5	0·915	0·77
34 50	285	198	261	164	0·917	0·83
39 40	266	221	244	197	0·918	0·89

Table III.

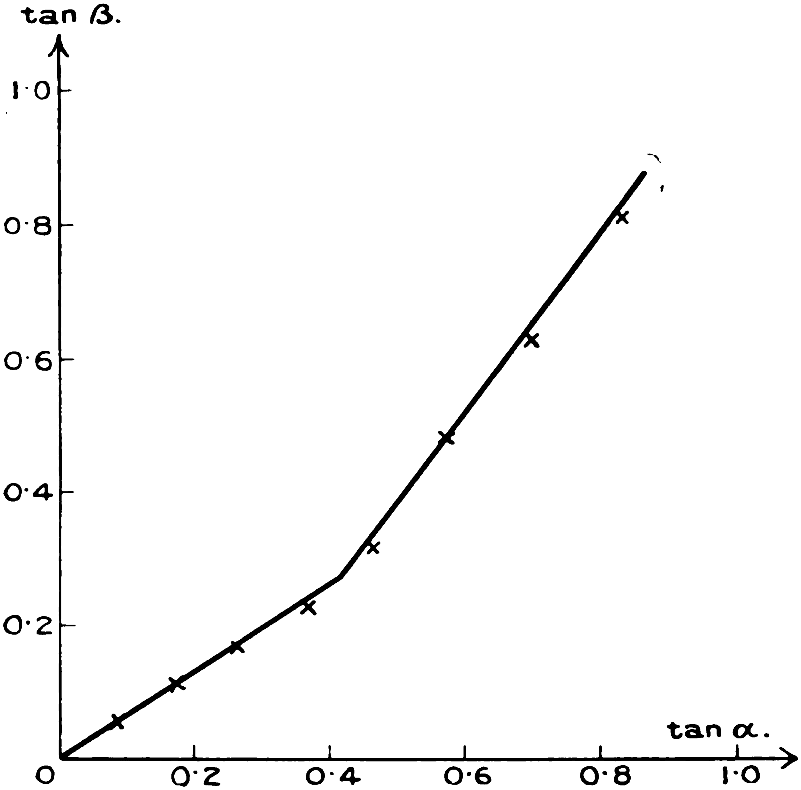
α.	*τ*.	tan *α*.	tan *β*.	$(T-t)/(N+n)$.
4° 45′	9	0·083	0·056	0·017
9 40	21	0·170	0·114	0·035
14 30	39	0·259	0·166	0·056
19 45	52	0·359	0·230	0·078
24 40	38	0·459	0·321	0·087
29 35	−34	0·568	0·479	0·068
34 50	−80	0·696	0·630	0·062
39 40	−139	0·829	0·808	0·046

Table IV.

α.	Error in *e*.	Error in *f*.	Error in *τ*.
9° 40′	±0·002	±0·021	±4·5
19 45	±0·003	±0·012	±5·3
29 35	±0·004	±0·012	±7·2

The regularity of the results for e indicates that the actual errors are considerably less than the limiting values here shown. But even if the errors are as great as these, the main conclusions are not affected.

Fig. 2.



Relations between the Angles of Incidence and Rebound.

In fig. 2 the relation between tan α and tan β is shown graphically. It will be seen that, although the conditions of the ordinary theory are violated, the relations predicted by it are verified. This is especially remarkable in view of the figures given in the last column of Table III. It there appears that the ratio of the tangential to the normal impulse increases with α until a critical value is reached, after which it shows a marked decrease. The maximum occurs at a point corresponding with the break in the graph in fig. 2. At this point slipping begins, and the lowest point of the ball moves forward after contact.

A determination of the coefficient of statical friction between the glass plate and the steel balls was made, the value obtained being 0·9. This corresponds closely with the greatest value of the ratio of the tangential and normal impulses.

Conclusions.

All the main features of the results given above were again observed in the experiments with other materials, with the exception that the drop in the ratio of the impulses aftor slipping occurred was less marked. The values of h and y showed a greater variation about the mean, and the final results were a little less regular, but they confirm the results for steel on glass in every particular.

The following statements may therefore be made with confidence :—

(1) Of the ordinarily accepted laws of rebound as stated in the introductory paragraph only the first is fully verified. e may be regarded as practically constant, but it increases slightly as the angle of incidence increases.

(2) The existence of a critical angle at which the law of rebound alters is also verified. This appears to happen when the ratio of the tangential to the normal impulse is slightly less than the coefficient of statical friction for the surfaces.

(3) For angles less than the critical angle the tangential impulse is much more than sufficient to bring the striking point of the ball to instantaneous rest. This point comes off the plane with a considerable *backwards* velocity.

(4) Before the critical angle is reached, the law is much more nearly expressed by the constancy of f, the ratio of the tangential velocity of the centre of the ball immediately after impact to that immediately before.

(5) For angles above the critical angle the ratio of the tangential to the normal impulse falls below the maximum value which it attains at the critical angle.

(6) The angles of incidence and rebound satisfy equations of the form

$$\tan\alpha = a\tan\beta, \qquad \text{for } \alpha < \alpha_0;$$

$$\tan\alpha = b\tan\alpha - c, \qquad \text{for } \alpha > \alpha_0.$$

If a, b, c, be regarded as constants to be determined by experiment for each kind of material and surface, these equations, combined with the constancy of e, may be regarded as giving the laws of rebound.

For angles less than the critical angle, constancy of e and f might be taken as an approximate law. It is possible that in this form the law may extend to impacts in which both bodies are in motion. Experiments on such impacts would be interesting, but are very difficult to carry out effectively.

We are indebted to Assistant Professor H. Klugh for permission to perform the above experiments in the Mechanics Laboratory of the City and Guilds (Engineering) College.

CI. *General Formulæ for Two Syntonized Coupled Circuits.*

By RAYMOND M. WILMOTTE, *B.A.*[*]

MUCH has been written on the subject of coupled circuits. There is, however, a connexion between a balanced four-armed bridge and two syntonized coupled circuits, which, as far as I am aware, has not been pointed out. This similarity permits the general formulæ for tuned syntonized coupled circuits being obtained from the equivalent capacity and inductance of the coupled circuits. From this the general conditions for the coupled circuits having only one resonant frequency can be readily obtained.

1. *General Case.*

Consider the four-armed bridge (fig. 1). Suppose the impedances Z_1, Z_2, Z_3, Z_4 are made up of resistances R_1, R_2, R_3, R_4 in series with reactances X_1, X_2, X_3, X_4 respectively. Then no current will flow in Z_0 when

$$Z_1/Z_4 = Z_2/Z_3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now, direct coupling between two circuits can be divided into three categories, in which the common reactance to both circuits is either in series with each circuit (as Z_0 in fig. 2), or in parallel to each circuit (as Z_0'), or a combination of both.

Fig. 2 can be redrawn as in fig. 3. The reactances X_1, X_2, X_3, X_4 of DC, DB, CE, BE are $L_1\omega$, $-1/C_1\omega$, $L_2\omega$, $-1/C_2\omega$ respectively, where $\omega/2\pi$ is the frequency.

---

[*] Communicated by the Author.

Fig. 1.

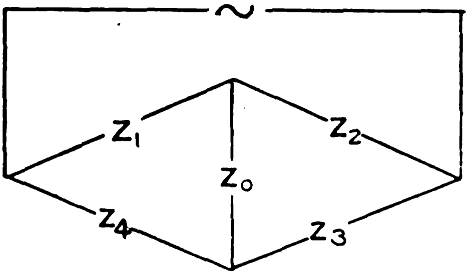


Fig. 2.

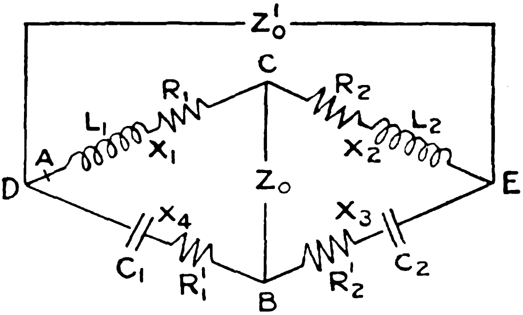
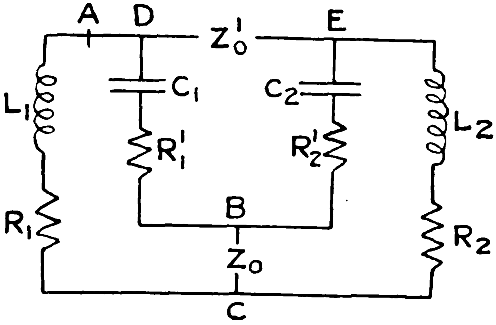


Fig. 3.



When the two circuits are syntonized, that is $L_1C_1=L_2C_2$, we have

$$X_1/X_4=X_2/X_3.$$

If at the same time

$$R_1/R_4=R_2/R_3, \quad . \; . \; . \; . \; . \; . \; . \; . \qquad (2)$$

the equation is equivalent to equation (1).

Hence, if R_1 and R_2 are small and can be neglected compared with $L_1\omega$ and $L_2\omega$, as is usually the case, the coupled circuits become equivalent to a balanced four-armed bridge irrespective of condition (2). Hence, an E.M.F. across BC will produce no current in DE. This would be accurately so if the resistances R_1' and R_2' of the condensers C_1 and C_2 were connected by the relation

$$R_1'/R_1 = R_2'/R_2. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Suppose an E.M.F. be applied across BC. Let I_a be the current at any point A in the primary circuit produced by this E.M.F., the reactance of the coupled circuits referred to the point A being X_a. Since no current flows in Z_0', X_a will be independent of Z_0'. Then the reactive power is $I_a^2 X_a$. Similarly, let I_b be the current at A when an E.M.F. is applied across DE, X_b being the reactance of the coupled circuits measured at A. In this case no current flows through Z_0, so that X_b will be independent of Z_0. The reactive power in this case is $I_b^2 X_b$. Now, since I_a is independent of I_b, the reactive powers can be added arithmetically.

If the current and equivalent reactance at A, when E.M.F.'s are applied simultaneously to BC and DE, are I and X respectively, we have, by equating the reactive powers,

$$W \equiv I^2 X = I_a^2 X_a + I_b^2 X_b. \quad . \quad . \quad . \quad . \quad (4)$$

Also it is evident that

$$I = I_a + I_b, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so that W is a minimum when

$$I_a X_a = I_b X_b.$$

Hence

$$X = \frac{X_a X_b}{X_a + X_b}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This could have been obtained *à priori*, for the equations (4) and (5) are the same as those for two reactances X_a and X_b in parallel.

From equation (6) we have that at resonance, that is when $X=0$, either

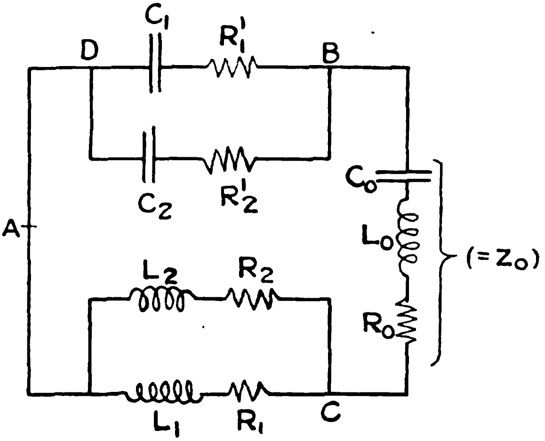
$$X_a = 0 \quad \text{or} \quad X_b = 0. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From this we see that at resonance, if an E.M.F. be applied at A, the current will be zero in either Z_0 or Z_0', and resonance can occur at two states, when $X_a=0$ and $X_b=0$, for X will then be zero. We shall see that X_a and X_b can be readily obtained for these conditions.

Let us first consider X_a. For this case the points D and

E are at the same potential and the circuit can be redrawn as in fig. 4. The most general case is obtained by putting a self-inductance L_0, a capacity C_0, and a resistance R_0 all in series for Z_0.

Fig. 4.



If we assume the resistances to be small compared with the reactances, with which they are connected in series, we can write immediately from the circuit the equivalent self-inductance, capacity, resistance, etc. of the coupled circuit, thus :—

$$\text{Equivalent self-inductance} \equiv L_a = \frac{1}{\frac{1}{L_1} + \frac{1}{L_2}} + L_0$$

$$= \frac{L_1L_2 + L_1L_0 + L_2L_0}{L_1 + L_2}. \qquad (8)$$

$$\text{Equivalent capacity} \equiv C_a = \frac{1}{\frac{1}{C_1 + C_2} + \frac{1}{C_0}}$$

$$= \frac{(C_1 + C_2)C_0}{C_1 + C_2 + C_0}. \quad . \quad . \qquad (9)$$

Hence

$$\text{Resonant frequency} \equiv \frac{1}{2\pi\sqrt{L_aC_a}}$$

$$= \frac{1}{2\pi\sqrt{\frac{[LC + L_0(C_1 + C_2)]C_0}{C_1 + C_2 + C_0}}}. \qquad (10)$$

In which, as before,

$$L_1C_1 = L_2C_2 = LC.$$

If the current in L_1 and C_1 is I_1, and that in L_2 and C_2 is I_2, then from fig. 4 it is evident that

$$I_1/I_2 = C_1/C_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and the current in Z_0 is (I_1+I_2).

The power dissipated is therefore

$$I_1^2(R_1+R_1') + I_2^2(R_2+R_2') + (I_1+I_2)^2R_0.$$

Hence the Equivalent resistance $\equiv R_a$

$$= \frac{(R_1+R_1'+R_0)C_2^2 + (R_2+R_2'+R_0)C_1^2 + 2C_1C_2R_0}{C_2^2}. \quad (12)$$

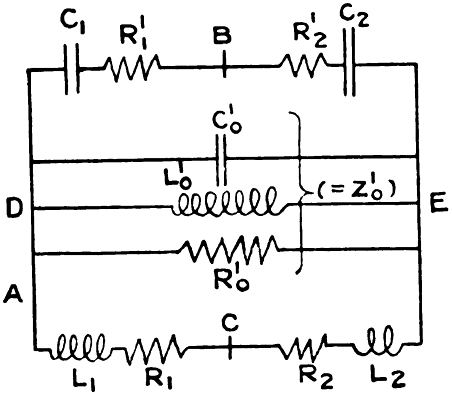
and

$$\text{Equivalent logarithmic decrement} = \frac{R_a}{2L_a n}, \quad . \quad (13)$$

where n is the frequency.

Treating X_b in the same way, we obtain fig. 5. Calling L_b, C_b, and R_b the equivalent self-inductance, capacity, and resistance respectively, measured at A of the coupled circuits, when no current flows through Z_0, we have for the most general case, in which Z_0' is made up of an inductance L_0', a capacity C_0', and a resistance R_0' (which is usually large compared with Z_0'), all in parallel,

Fig. 5.



$$L_b = \cfrac{1}{\cfrac{1}{L_1+L_2} + \cfrac{1}{L_0'}}$$

$$= \frac{(L_1+L_2)L_0'}{L_1+L_2+L_0'}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$C_b = \frac{1}{\frac{1}{C_1} + \frac{1}{C_2}} + C_0'$$

$$= \frac{C_1C_2 + C_1C_0' + C_2C_0'}{C_1 + C_2} \quad . \; . \; . \; . \; . \; . \quad (15)$$

$$\text{Resonant frequency} \equiv \frac{1}{2\pi\sqrt{L_b \, . \, C_b}}$$

$$= 2\pi \frac{1}{\sqrt{\frac{LC \, . \, L_0'}{L_1 + L_2 + L_0'}\left[1 + \frac{C_0'}{C_1} + \frac{C_0'}{C_2}\right]}} .$$

If I_1' is the current in L_1 and L_2, and I_2' is the current in C_1 and C_2,

$$I_1'/I_2' = 1/LC\omega^2. \quad . \; . \; . \; . \; . \; . \quad (17)$$

Inserting the value for the resonant frequency, this becomes

$$I_1'/I_2' = L_0'\left(1 + \frac{C_0'}{C_1} + \frac{C_0'}{C_2}\right)\bigg/(L_1 + L_2 + L_0'). \; . \; . \quad (18)$$

Also the current I_0' in R_0' is given by

$$I_0' = I_1' \frac{(L_1 + L_2)\omega}{R_0'} .$$

Hence the power dissipated is

$$I_1'^2(R_1' + R_2') + I_2'^2(R_1 + R_2) + R_0'I_0'^2,$$

from which we have

$$R_b = R_1 + R_2 + \frac{R_1' + R_2'}{L^2C^2\omega^4} + \frac{(L_1 + L_2)^2\omega^2}{R_0'}, \quad . \quad (19)$$

and the equivalent logarithmic decrement $= \frac{R_b}{2L_b \, . \, n}$ . . (20)

For the general case of fig. 2 there are two possible sets of constants for the resonant frequency. One is given by L_a, C_a, R_a, etc. of equations (1) to (13), and the other by L_b, C_b, R_b, etc. of equations (14) to (20). From these equations any case of direct coupling can be calculated at the resonant frequencies, if the following conditions hold :

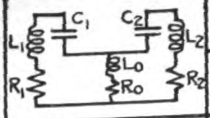
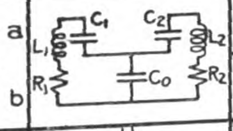
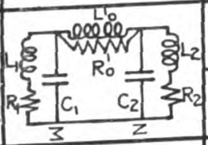
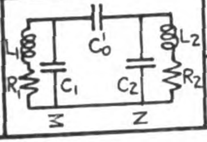
$$R_1/R_1' = R_2/R_2'$$

and

$$L_1C_1 = L_2C_2 \equiv LC.$$

The first condition seldom holds, but this does not invalidate the theory, which will apply very approximately, if the resistances are small compared with their corresponding reactances, as is almost invariably the case.

TABLE I.

No.	Circuit.	Conditions	Inductance.	Capacity.	Resistance.	Logarithmic Decrement.	Resonant Frequency.
1 a	 L_1 C_1 C_2 L_2 L_0 R_1 R_0 R_2	$C_0=\infty$	$\frac{L_1L_2+L_1L_0+L_2L_0}{L_1+L_2}$	C_1+C_2	$R_1+R_2\left(\frac{C_1}{C_2}\right)^2+\left(\frac{C_1+C_2}{C_2}\right)^2R_0$	$\frac{R_1L_1^2+R_2L_2^2+R_0(L_1+L_2)^2}{2(L_1L_2+L_1L_0+L_2L_0)\frac{L^2n}{L_1+L_2}}$	$\frac{1}{2\pi\sqrt{LC+L_0(C_1+C_2)}}$
b		$L_0'=\infty$ $C_0'=0$ $R_0'=\infty$	L_1+L_2	$\frac{C_1C_2}{C_1+C_2}$	R_1+R_2	$\frac{R_1+R_2}{2(L_1+L_2)n}$	$\frac{1}{2\pi\sqrt{LC}}$
2 a		$L_0=0$ $R_0=0$	$\frac{L_1L_2}{L_1+L_2}$	$\frac{(C_1+C_2)C_0}{C_1+C_2+C_0}$	$R_1+R_2\left(\frac{C_1}{C_2}\right)^2$	$\frac{(R_1L_1^2+R_2L_2^2)(L_1+L_2)}{2L_1^3L_2n}$	$\frac{1}{2\pi\sqrt{LC\cdot\frac{C_0}{C_1+C_2+C_0}}}$
b		$L_0'=\infty$ $C_0'=0$ $R_0'=\infty$	L_1+L_2	$\frac{C_1C_2}{C_1+C_2}$	$R_1\ R_2$	$\frac{R_1+R_2}{2(L_1+L_2)n}$	$\frac{1}{2\pi\sqrt{LC}}$
3 a	 L_0' L_1 R_0' L_2 R_1 C_1 C_2 R_2 M N	$L_0=0$ $C_0=\infty$ $R_0=0$	$\frac{L_1L_2}{L_1+L_2}$	C_1+C_2	$R_1+R_2\left(\frac{C_1}{C_2}\right)^2$	$\frac{(R_1L_1^2+R_2L_2^2)(L_1+L_2)}{2L_1^3L_2n}$	$\frac{1}{2\pi\sqrt{LC}}$
b		$C_0'=0$	$\frac{(L_1+L_2)L_0'}{L_1+L_2+L_0'}$	$\frac{C_1C_2}{C_1+C_2}$	$R_1+R_2+\frac{(L_1+L_2)^2\omega^2}{R_0'}$	$\frac{R_0'(R_1+R_2)+(L_1+L_2)^2\omega^2}{2R_0'(L_1+L_2)\frac{L_0'n}{L_1+L_2+L_0'}}$	$\frac{1}{2\pi\sqrt{LC\frac{L_0'}{L_1+L_2+L_0'}}}$
4 a	 L_1 C_0' L_2 R_1 C_1 C_2 R_2 M N	$L_0=0$ $C_0=\infty$ $R_0=0$	$\frac{L_1L_2}{L_1+L_2}$	C_1+C_2	$R_1+R_2\left(\frac{C_1}{C_2}\right)^2$	$\frac{(R_1L_1^2+R_2L_2^2)(L_1+L_2)}{2L_1^3L_2n}$	$\frac{1}{2\pi\sqrt{LC}}$
b		$L_0'=\infty$ $R_0'=\infty$	L_1+L_2	$\frac{C_1C_2+C_1C_0'+C_2C_0'}{C_1+C_2}$	R_1+R_2	$\frac{R_1+R_2}{2(L_1+L_2)n}$	$\frac{1}{2\pi\sqrt{LC\left(1+\frac{C_0'}{C_1}+\frac{C_0'}{C_2}\right)}}$

In Table I. is given a list of special cases, in which the symbols are the same as have been used throughout. A point to be noticed in circuits 3 and 4 is that another impedence could be inserted between the points M and N; the effect on the formulæ would be to replace the coupling reactance by the sum of the two coupling reactances. Thus, if L_0'' and L_0''' were the coupling inductances in circuit 3, the formulæ would hold if $(L_0''+L_0''')$ were substituted for L_0'. Similarly, for circuit 4 it would be necessary to write

$$\frac{C_0''C_0'''}{C_0''+C_0'''} \text{ for } C_0'.$$

2. *Conditions for Single Frequency.*

In certain cases using pure reactance coupling it is possible to obtain the condition that the two resonant frequencies are equal so that the circuit has apparently only one resonant frequency.

From equations (10) and (16) we see that the general condition for this to occur is given by

$$\frac{[LC+L_0(C_1+C_2)]C_0}{C_1+C_2+C_0}=\frac{LC\,.\,L_0'}{L_1+L_2+L_0'}\left[1+\frac{C_0'}{C_1}+\frac{C_0'}{C_2}\right]. \qquad (21)$$

In Table II. four special cases are given.

The peculiar property of circuit 5 of giving only one resonant frequency was first mentioned by Eccles and Makower in a paper to the British Association in 1915 *. It will be seen that it is far from being the only case in which a single resonant frequency is obtainable when the resistances are small.

3. *Limitations.*

The method explained above only applies to forms of coupled circuits which can be represented by a balanced four-armed bridge. Thus, if circuit 1 of Table I. is adjusted so that

$$(L_0+L_1)C_1=(L_0+L_2)C_2, \quad . \quad . \quad . \quad . \qquad (22)$$

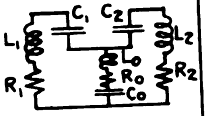
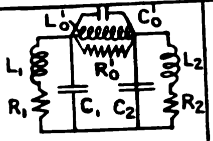
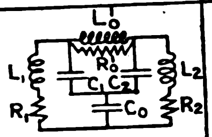
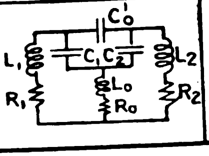
the method fails. This particular case is unfortunately of importance, for it is equivalent to the simple induction circuit.

In a straight induction circuit part of the lines of force link both circuits, and part (called the stray flux) link only one or other of the two circuits. If this stray flux produces

---

* 'Electrician,' vol. lxxv. p. 905 (1915).

TABLE II.

No.	Circuit.	Conditions.	Resonant Frequency.
5		$L_0C_0 = LC$	$\frac{1}{2\pi\sqrt{LC}}$
6		$L_0'C_0' = LC.$	$\frac{1}{2\pi\sqrt{LC}}$
7		$\frac{L_0'}{C_0} = \frac{LC}{C_1C_2}$	$\frac{1}{2\pi\sqrt{LC\ \frac{L_0'}{L_1+L_2+L_0'}}}$
8		$\frac{L_0}{C_0} = \frac{LC}{C_1C_2}$	$\frac{1}{2\pi\sqrt{LC+L_0(C_1+C_2)}}$

self-inductances L_1 and L_2 in the two circuits respectively, and the mutual inductance is M_0, the circuits become evidently equivalent to circuit I, in which L_0 is replaced by M_0. Usually, however, the circuits are syntonized according to condition (22). For this case, then, the method fails, but it would of course hold if the conditions were such that

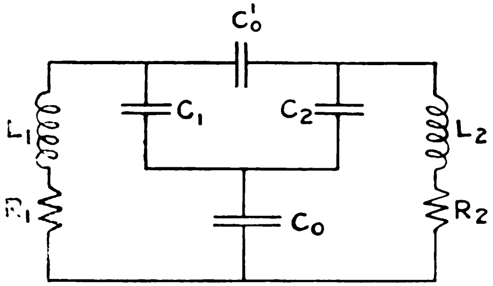
$$(L_1'-M_0)C_1=(L_2'-M_0)C_2,$$

where L_1' and L_2' are the self-inductances of each circuit respectively when no current flows in the other.

4. *Experimental Verification.*

To test the theory experimentally a circuit, as shown in fig. 6, was set up. This was loosely coupled to an oscillator, and the current flowing in L_1, L_2 and C_0' measured as the frequency was altered. The coupling remained unaltered, and it was ascertained that the current in the source remained very nearly constant over the range of frequency used. It was found, as expected, that near the higher resonant frequency the value of C_0' could be altered without affecting the current in the parts of the circuit, and at resonance C_0' could actually be short-circuited without producing any appreciable effect. Near the lower resonant frequency the same was true with regard to C_0.

Fig. 6.



Two such circuits, having constants given in Table III., were examined. The currents I_1, I_2, I_0, I_0' in the inductances L_1, L_2 and condensers C_0, C_0' respectively were measured at the two resonant frequencies. The results are shown in Table IV., where they can be compared with the calculated values.

It will be seen that the agreement is well within the experimental error, when one considers that the frequency was about half a million and that the thermo-junction and

TABLE III.

(The opposite capacities are given in micromicrofarads.)

Circuit.	C_1.	C_2.	C_0.	C_0'.	LC.
A.........	1000	2274	20000	50	$0{\cdot}112 \times 10^{-12}$
B.........	1195	500	5000	250	$0{\cdot}0592 \times 10^{-12}$

TABLE IV.

Circuit A.

	Higher Frequency.		Lower Frequency.	
	Observed.	Calculated.	Observed.	Calculated.
I_2/I_1	0·44	0·438	0·99	1·000
I_0/I_1	3·2	3·28	0	0
I_0'/I_1	0	0	0·08	0·067
Frequency ...	511,000	513,000	458,000	458,000

Circuit B.

	Higher Frequency.		Lower Frequency.	
	Observed.	Calculated.	Observed.	Calculated.
I_2/I_1	0·43	0·418	1·00	1·000
I_0/I_1	1·42	1·418	0	0
I_0'/I_1	0	0	0·42	0·415
Frequency ...	754,000	757,000	503,000	502,000

heater (of the non-contact type) had to be moved from one position in the circuit to another without altering the shape of the circuit in any way.

It was also found that, though the E.M.F. induced in the circuit was greater at the higher frequency, the value of I_1 was less. That is because the effective resistance at the higher frequency is greater than at the lower, as will be seen on examining Table I., the two cases that occur being 2 *a* and 2 *b*.

Circuit 8 (Table II.) was also set up and adjusted to give a single frequency. The constants of the circuit were as follows:—$C_1 = 1000\,\mu\mu\,F$, $C_2 = 2830\,\mu\mu\,F$, $C_0'=470\,\mu\mu\,F$, $L_0 = 11\,\mu\,H$, $LC = 0{\cdot}060\times10^{-12}$. The inductance L_0 was placed near the shield of a condenser, and it is probable that its effective value was appreciably decreased thereby.

As it was, the condition $L_0/C_0'=LC/C_1 . C_2$ for a single frequency did not quite hold, for $L_0/C_0' = 0{\cdot}023$ and $LC/C_1 . C_2=0{\cdot}021$. The agreement is not bad, but not perfect. By putting $L_0=10\,\mu\,H$ perfect agreement would be obtained. The resonant frequency of this circuit was found to be 512,000, which compares well with the calculated value of 510,000.

4. *Conclusion.*

In conclusion, I would like to mention that for any given case it is probably easier to make use of the principle explained above for finding the equivalent constants of two syntonized coupled circuits at their resonant frequencies rather than substitute particular values in the somewhat cumbrous general expressions obtained. It will be found that for the cases to which the method applies it is much easier than the ordinary method of writing down the equations for the currents in the various branches of the net-work.

August 1925.

CII. *The Ranges of Secondary β-Rays.* *By* J. M. NUTTALL, *M.Sc., Senior Lecturer in Physics, University of Manchester, and* E. J. WILLIAMS, *M.Sc., Fellow of the University of Wales* *.

1. *Introduction.*

THE cloud method of photographing the tracks of ionizing particles, due to Professor C. T. R. Wilson, F.R.S., provides a means of determining the lengths of β-rays, free from difficulties arising from the scattering of the rays. The latter effect is very pronounced in the case of β-rays which have initial energies of the order of those of the rays produced by the photoelectric action of X-rays, and in other methods of making observations it is impossible to deal with the total distance traversed by these electrons. Theories of the decrease of velocity of electrons passing through matter deal with the total distance travelled, and it is important that this quantity should be observed. This is possible using Wilson's cloud method, since it records the actual path of the electron up to the point where it ceases to ionize the gas. This point can be taken as a convenient definition of the *end* of the ray, and the distance travelled up to this point as the *range* of the ray.

Previous measurements of the lengths of β-ray tracks, obtained by the cloud method, have been made by C. T. R. Wilson † and by H. Ikeuti ‡. Wilson measured the ranges in air of the rays produced by the characteristic X-rays of copper and silver respectively, and Ikeuti determined the range in air of the rays produced by X-rays of wave-length 0·21 Å. The results obtained by these observers are in accordance with Whiddington's law which states that the range of a β-ray is proportional to the square of its initial energy. P. Auger § has also made observations on the lengths of certain β-rays produced in a mixture of hydrogen and small quantities of the rare gases, in an investigation of the phenomenon of the production of "paired" β-rays, *i. e.*, two rays having a common origin. In the theory of this phenomenon one of the two rays is assumed to be produced by the absorption of a quantum of the primary X-rays, and the other (called the "tertiary ray") by the absorption of the quantum of fluorescent X-rays subsequently emitted by the same atom. Auger finds that the relative

---

* Communicated by Prof. W. L. Bragg, F.R.S.

† C. T. R. Wilson, Proc. Roy. Soc. A, civ. p. 1 (1923).

‡ H. Ikeuti, *Comptes Rendus*, clxxx. p. 1257 (1925).

§ P. Auger, *Journal de Physique*, vi. No. 6, p. 205 (1925).

values of the ranges of the tertiary rays produced in different rare gases can be satisfactorily explained on the above-mentioned theory of their origin provided Whiddington's law holds. In the work of Wilson and Auger the β-rays measured are produced by fluorescent X-radiations. The K and L radiations of an element differ in wave-length by about 15 per cent., and therefore produce β-rays possessing initial energies differing to the same extent, and this makes an accurate interpretation of the results obtained in such cases difficult. Again, in all the experiments referred to the β-rays are produced in gaseous mixtures, which means that there will be further inequalities in the initial energies due to the different ionization potentials of the constituent elements.

In the present experiments simple gases have been used as far as possible, and the β-rays have been produced by homogeneous X-rays reflected from a crystal. Observations have been made on the β-rays produced in oxygen, nitrogen, hydrogen, and argon by X-rays of wave-lengths ranging from 0·41 Å to 1·54 Å. The results obtained and described in this paper show how the range of β-rays in a given gas varies with the initial energy of the rays, and also how the range depends on the nature of the gas.

2. *Experimental Method.*

The experimental arrangement used for the production and photographing of the β-rays has been fully described in a previous paper [*] by the authors on "β-rays associated with scattered X-rays," and it is only necessary here to point out that in all the experiments homogeneous X-rays, obtained by reflexion from a crystal, were used to produce the β-rays, and that in all cases stereoscopic photographs were taken in order that measurement of the lengths of the β-ray tracks in space might be made. The lengths of the tracks were obtained from the stereoscopic photographs by replacing the photographic plates in the camera, illuminating them, and tracing out the common image, which coincides in space with the original track provided the adjustment of the camera is exactly the same as when the photographs were taken.

3. *Initial Energies of the β-rays.*

The initial energy, E, of the β-rays produced by the photoelectric action of radiation of frequency ν is given by Einstein's photoelectric equation

$$E = h\nu - \epsilon,$$

---

[*] Nuttall & Williams, Phil. Mag. i. p. 1217 (1926).

ϵ being the energy lost by the photoelectron in escaping from the atom. It is almost impossible in the cases of oxygen, nitrogen, and argon to ascertain from the β-ray track the energy-level in the atom from which the photoelectron is ejected. The value of ϵ, even for the most firmly bound electrons, is, however, in all these cases small compared with the energies of the X-ray quanta concerned, and a sufficiently accurate value of the effective binding energy can be deduced from the following considerations. The magnitude of the discontinuity in the absorption of X-rays by an element as the wave-length of the X-rays passes the K absorption limit for that element, and the nature of the variation of the absorption with wave-length on either side of the limit, indicate that for radiation of wave-length less than that corresponding to the K absorption limit, the absorption by the K electrons is about 6/7ths of the total absorption. The magnitude of the L discontinuity shows that the greater part of the remaining absorption is due to the L electrons. As ϵ is small compared with $h\nu$, its effective value can therefore be taken as $(6/7\epsilon_K+1/7\epsilon_L)$, where ϵ_K and ϵ_L are the binding energies of the K and L electrons respectively. This is the effective value of ϵ used in calculating the initial energies of the β-rays, equation (1) becoming

$$E=h\nu-6/7\epsilon_K-1/7\epsilon_L. \quad . \quad . \quad . \quad . \quad (1\,a)$$

In the case of the β-rays produced in a mixture of hydrogen and a small quantity of argon the paired tracks, according to Auger *, consist of a β-ray ejected from the K level of argon and another ray due to the absorption by the same atom of the K fluorescent quantum subsequently emitted, which has a range of about 1 mm. Assuming the interpretation to be correct, we can distinguish the β-rays which originate in the K level of argon when argon is present in small quantities in an atmosphere of hydrogen. In the present experiments this has been done in the case of β-rays produced in such a mixture by X-rays of wave-length 1·54 Å, the initial energy in volts of the rays considered being 4800, as compared with an average initial energy of 7560 volts for β-rays ejected from oxygen atoms by the same radiation. The difference is appreciable, and by measuring the length of these rays additional information can be obtained about the β-rays in hydrogen without using radiation of a different wave-length.

---

* *Loc. cit.*

4. *Range in Gaseous Mixtures.*

It can be readily shown that if the variation of range with initial energy obeys the same law in different gases $g_1, g_2 \ldots g_n$, then the range r_m of a β-ray in a mixture of these gases is given by

$$\frac{1}{r_m}=\frac{p_1}{r_1}+\frac{p_2}{r_2}+\ldots\frac{p_n}{r_n}, \quad . \quad . \quad . \quad . \quad (2)$$

where r_n is the range of the β-ray in the gas g_n when its pressure and temperature are the same as those of the mixture, and p_n is the partial pressure of the gas g_n in the mixture expressed as a fraction of the total pressure of the mixture.

In all experiments using the cloud method, water-vapour is essentially present in the cloud chamber where the β-rays are produced, and the correction necessary in order to obtain the range in the pure gas concerned has been made by applying equation (2). In the cases of oxygen, nitrogen, and argon this correction is very small, being in no case greater than 1 per cent. In the case of hydrogen it is more appreciable, being of the order of 10 per cent. The condition of application of equation (2) is in all cases considered to be sufficiently well satisfied to ensure corrections of the necessary accuracy.

5. *Results.*

The results obtained in the present experiments are shown in Table I.

Column 1 gives the nature of the gas in the cloud chamber, column 2 the wave-length of the X-rays used to produce the secondary β-rays, and column 3 the number of β-ray tracks measured in each case.

The initial energy of the β-rays, calculated from equation (1 *a*), is given in column 4 and is stated in *volts* (V). Column 5 gives the mean range (in cm.) of the β-rays at 0° C. and 76 cm. pressure. It might be pointed out here that the ranges of the separate β-ray tracks for any given initial energy vary between fairly wide limits ($\pm$ 30 per cent. of the mean value), but that in taking a series of measurements the mean value is only altered by very small amounts after about eight tracks have been examined. In most cases about twenty tracks were measured, and in general it was found that the shorter tracks were those of β-rays which had suffered most deflexions. The 6th column gives the value of R/V^2 in each case, and column 7 gives the mean value of R/V^2 for a given gas.

TABLE I.

GAS.	Wave-length of exciting X-rays in Å.	No. of tracks examined.	Initial energy of β-rays expressed in volts (V).	Mean range of β-rays in cm. at N.T.P. (R).	$\frac{R}{V^2} \times 10^9$.	Mean values of $\frac{R}{V^2} \times 10^9$.	Atomic stopping-power of gas.	Atomic No. of gas.
Oxygen O_2 ...	1·54	35	7,560	·101	1·76	1·75	(8)	8
,, ...	·709	15	16,910	·49	1·71			
,, ...	·614	19	19,590	·67	1·76			
,, ...	·545	22	22,130	·87	1·78			
Nitrogen N_2	·614	19	19,700	·77	1·98	2·01	7·0	7
,,	·545	22	22,240	1·01	2·05			
Argon A_1 ...	·614	20	17,220	·48	1·62	1·63	17·0	18
,, ...	·545	20	19,760	·65	1·66			
,, ...	·41	6	27,190	1·20	1·62			
Hydrogen H_2	1·54	20	7,560	·73	12·71	14·2	1·0	1
,,	1·54	15	4,800	·36	15·63			

6. *The Variation of Range with the Initial Energy of the β-ray.*

According to Whiddington* the range of a β-ray is proportional to the square of its energy or, in terms of our foregoing nomenclature, $R \propto V^2$. The results given in column 6 of Table I. show that this law holds with a high degree of accuracy for β-rays produced by X-rays of wave-lengths ·41–1·54 Å in oxygen, nitrogen, and argon. The initial energies of these β-rays range from 7,560 to 27,190 volts and in the case of oxygen, for instance, the results cover a nine-fold variation of the range of the rays. The slight deviation in the two values of R/V^2 in the case of hydrogen may be due to uncertainty in the calculation of V, the initial energy of the rays, since here the values of the binding energies of the ejected electrons are of more relative importance than in the other cases, and this is especially so in the case of the rays for which V is estimated as 4,800.

7. *Variation of Range of β-rays with Nature of the Gas.*

It is seen from column 7 of the Table (which gives the mean values of R/V^2 for a given gas) that the range of a β-ray of given initial energy varies with the nature of the gas in which it has been observed, being greater the lower the atomic number of the gas. The mean value of R/V^2 gives a measure of the reciprocal of the molecular stopping power of the gas. In order to obtain the atomic stopping power we must take into account the monatomic or diatomic nature of the gas. The stopping powers per atom for the different gases are given in column 8 of the Table, the value for oxygen being arbitrarily chosen as (8). The mean stopping powers of the atoms of nitrogen, argon, and hydrogen then become 7, 17, and 1 respectively, Thus the relative atomic stopping powers of the gases are approximately proportional to their atomic numbers or to the number of extra-nuclear electrons per atom, as given in the last column. We may therefore conclude that R is proportional to $\frac{1}{N}$, where N is the atomic number of the gas and R is the range in the gas at a given atomic concentration, of β-rays of given initial energy.

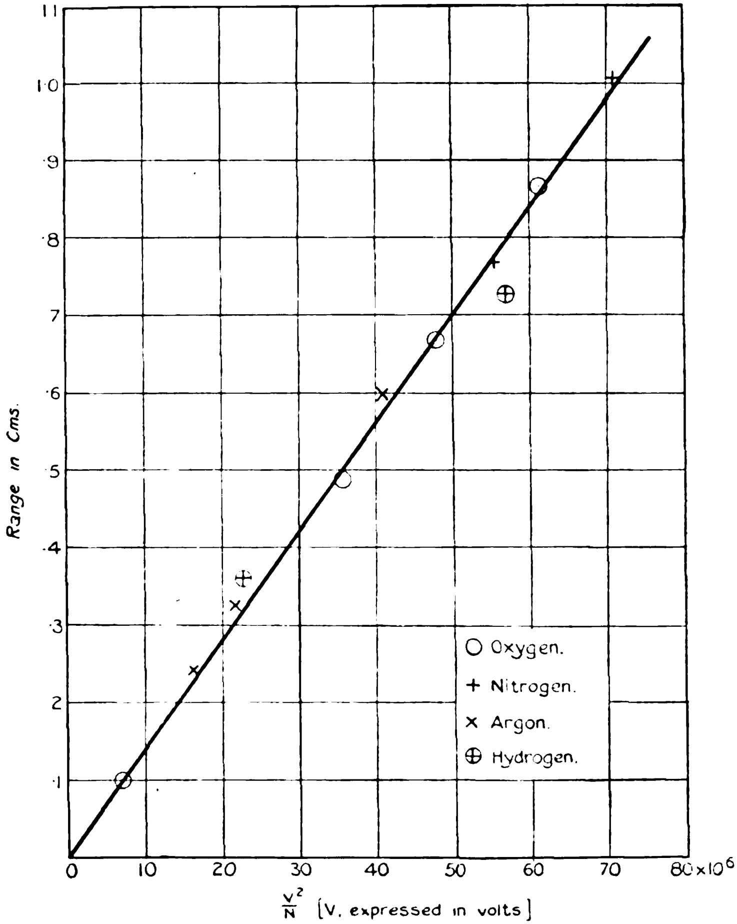
The two laws connecting the range of the secondary β-rays with initial energy and atomic number of the gas traversed respectively can be expressed by the relation

---

* R. Whiddington, Proc. Roy. Soc. A, lxxxvi. p. 360 (1912).

$$R = K \frac{V^2}{N},$$

where K is a constant and R is the range in the gas at a given *atomic* concentration. For an atomic concentration equal to that in a diatomic gas at N.T.P. the numerical value of K which represents the present results is $1{\cdot}42 \times 10^{-8}$.



The extent to which the ranges of the β-rays produced in the different cases investigated in the present work obey this law can be realized from the figure. The values of R for the gas at atomic concentration equal to that of a diatomic gas at N.T.P. is plotted along the axis of abscissæ and the value of V^2/N along the axis of ordinates. If the law was accurately obeyed all the points would lie on a straight line through the origin. The straight line drawn corresponds to the value of K given above.

The theoretical significance of the results described in this paper are being considered and it is hoped to publish an account of the results in the near future.

8. *Summary.*

The Wilson cloud method has been used to photograph the tracks of secondary β-rays produced by a beam of homogeneous X-rays of known wave-length in the gases oxygen, nitrogen, argon, and hydrogen. The stereoscopic photographs of the β-ray tracks have been examined and measured and the ranges of the β-rays at N.T.P. deduced.

It is found that for any one gas, the range of the β-ray is proportional to the square of its initial energy (Whiddington's law), the agreement holding over a range of energies from 4,800–27,190 volts. It is also found that the range of the β-ray varies as the reciprocal of the atomic number of the gas, for equal atomic concentrations. Both these relations are included in the law expressed by $R=KV^2/N$, K being a constant and having the value $1{\cdot}42\times10^{-8}$ when R is the range in a gas at atomic concentration equal to that of a diatomic gas at N.T.P.

In conclusion the authors desire to express their thanks to Professor W. L. Bragg, F.R.S., for his interest and helpful suggestions during the progress of the work.

Physical Laboratories,
Manchester University.
August 1926.

CIII. *Notes on Scattered X-Rays. The J Phenomenon* (Part V.). *By* Prof. C. G. Barkla, *F.R.S., and* Gladys I. Mackenzie, *M.A., B.Sc., University of Edinburgh**.

In an earlier paper† we described two alternative ways in which the beams of X-rays scattered in directions making angles at 60° and 120° with the primary radiation differed from one another. In one case the beam at 120° was absorbed at the same rate as the beam at 60°; but the intensity of the former, as measured by ionization in a short electroscope, dropped suddenly when the heterogeneous beam by filtering reached certain critical penetrating powers. These were the J_1, J_2, J_3 discontinuities shown by the radiation scattered at 120° and not by that scattered at 60°.

---

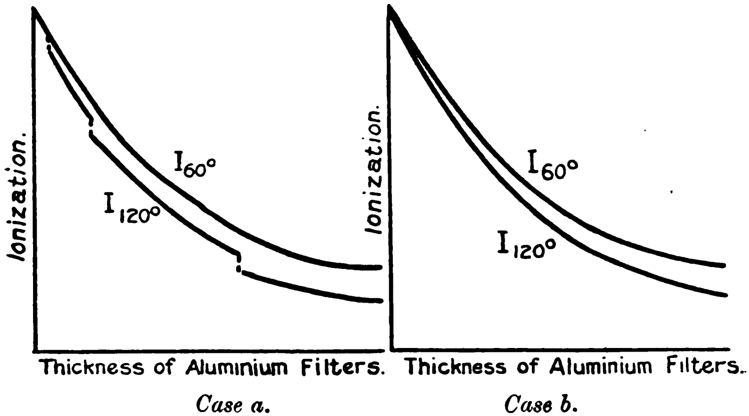
* Communicated by the Authors.

† "Notes on the Superposition of X-rays and on Scattering. The J Phenomenon (Part III.)." Phil. Mag. Feb. 1926.

In the other case the beam at 120° appeared continuously more absorbable than that at 60°, giving the superficial appearance of the Compton difference of wave-length with angle of scattering.

In the one case, *Case a*, as the beams were transmitted through aluminium, and by filtering reached higher and higher *average* frequencies, there appeared three strongly-marked "absorption lines" in the beam at 120°, but not in the beam at 60°. In the other case, *Case b*, instead of showing "absorption lines" the beam at 120° was continuously more absorbable than that at 60°. It was already in the region beyond an "absorption edge."

Fig. 1.

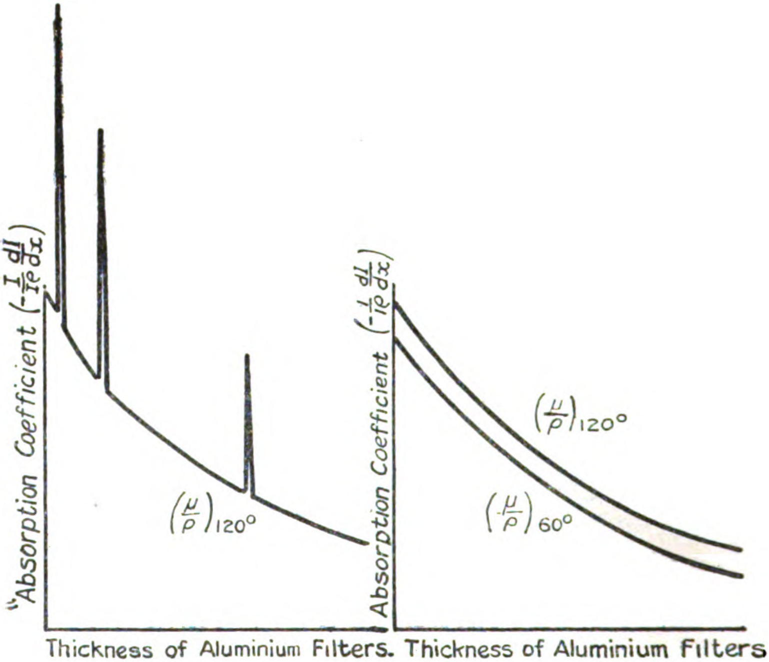


Case a. *Case b.*

These results are indicated in figs. 1 and 2. In fig. 1 ionization is plotted against thickness of intercepting aluminium; $I_{120°}$ showing the steps, $I_{60°}$ showing steadily decreasing intensity in *Case a*. In the alternative case, *Case b* (Exper. 13 in previous paper), neither beam showed any discontinuity by successive filtering, but $I_{120°}$ fell more rapidly than $I_{60°}$, that is the former was more absorbable.

In fig. 2 absorption-coefficients [or more accurately $-\frac{1}{I\rho}\frac{dI}{dx}$, where I is the ionization] are plotted against the thickness of aluminium, the beam at 120° showing the peaks, but that at 60° giving a smooth curve in *Case a.* The other case is shown on the right side of the figure with no unusual features, but the beam at 120° has a steadily higher "absorption-coefficient."

Fig. 2.



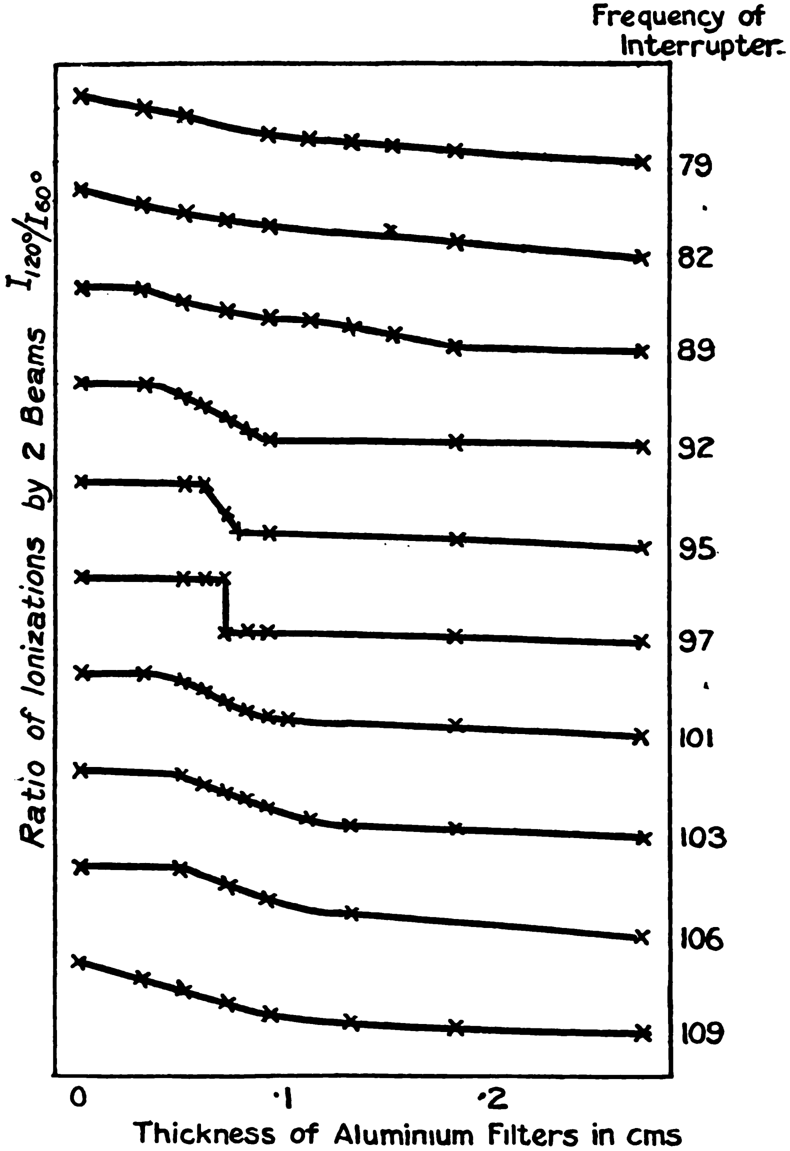
Case a. *Case b.*

At the time of these experiments there was no indication of the cause of the difference between the two results, or of the factors which determined whether the result of the experiment should be (*a*) or (*b*). It had, however, been made clear that these were of a nature never previously taken into consideration, and that the distinctive feature was the dependence on some sort of average constitution of the whole heterogeneous beam, and not on any particular constituent frequency, or even simple combination of frequencies. A systematic search of the cause of the variable result showed at once that it depended on the details of the process of excitation of the X-rays. The X-ray tube was excited by an induction coil with mercury jet interrupter. The frequency of interruption of the primary current was varied, and experiments were performed in the manner previously described. It was seen that *Case a*, showing discontinuities, gradually merged into *Case b*, showing a steady difference of absorbability as the frequency of interruption was changed. More precisely *Case a*, showing very abrupt discontinuities, was produced at only a very definite frequency of interruption, or over a very narrow range of frequencies; with lower and higher frequencies the width of the "absorption line" increased rapidly until it spread through the whole of the absorbability spectrum, and *Case a* had become *Case b*. Thus fig. 3 gives the ratio of $I_{120^\circ}/I_{60^\circ}$ for various thicknesses of absorbing aluminium and for frequencies of interruption varying from 79 to 109 per second. At a frequency 97 per second the change in ionization was most abrupt.

Thus by change of frequency of the interrupter the "absorption lines" of fig. 2 become wider and less strongly marked absorption-bands, until the band covers the whole range of the absorbability spectrum, which is then *Case b* (fig. 2). *Case b* was thus connected up to *Case a* by a continuous series of results. The frequency of the interrupter is, of course, not the fundamental factor; indeed, with another X-ray tube the critical frequency was not 97 but considerably over 100. And later still, after many alterations, only *Case b* appeared throughout the whole range of frequencies, as is shown in fig. 4, obtained with the same tube. Cases *a* and *b* are only widely-separated forms of exactly the same phenomenon—a conclusion to which we were led by experiments of a different kind. Thus, again, what superficially appeared to support Compton's theory was shown to be no other than the J phenomenon appearing in the scattered radiation.

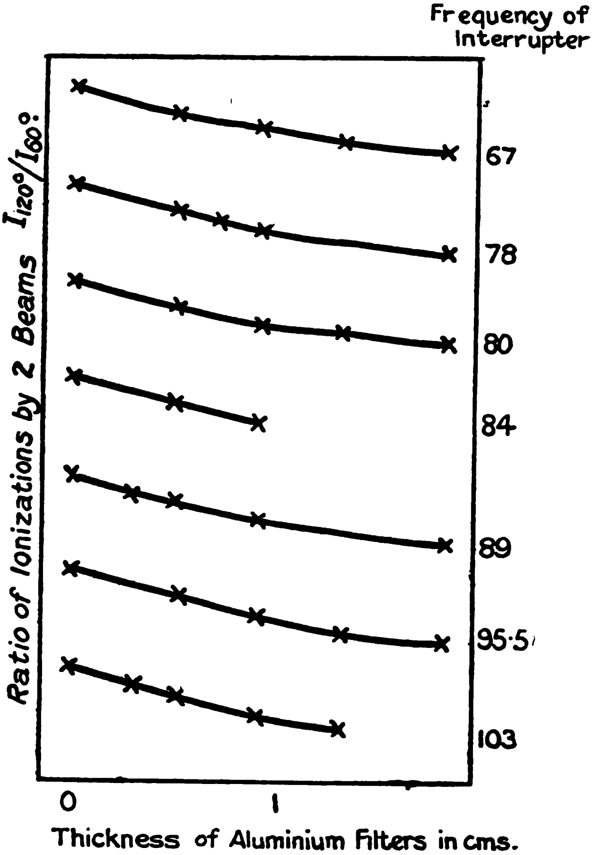
The further discussion of the conditions essential to the appearance of a discontinuity will be given later. Our main purpose at present is to record the fact that the factor which decides the degree of activity due to a complex beam acting as a whole is to be found in the details of the method of excitation of the X-rays; that is, it is determined by the large-scale structure of the radiation and not by its constituent frequencies. It might be expected that the more

Fig. 3.



continuous (the less intermittent) is a stream of radiation, the higher is the degree of coherence it will show. And though the magnitudes considered as providing a sufficient degree of homogeneity in the radiation are large compared with a wave-length, they are probably minute compared with those associated with a frequency of one hundred or thereabouts. But the material necessary for a profitable discussion of these questions has not yet been fully published.

Fig. 4.



It might be recorded that the variable factor appears to have been eliminated by Dr. W. H. Watson in this laboratory, working with an alternator-transformer and Coolidge tube. Results will shortly be published. The variations of potential supplied by a coil and interrupter are naturally much less regular than those from such an alternator-transformer.

CIV. *The Control of the J Phenomenon* (Part VI.). *By* Prof. C. G. **Barkla** *and* Dr. W. H. **Watson**, *University of Edinburgh*[*].

THE conditions determining the nature and properties of a beam of X-rays have hitherto not been sufficiently under control to enable us to ensure the certain occurrence of the J discontinuities in the activity of the radiation studied. The apparently capricious nature of the phenomenon, when its occurrence under a wide variety of conditions was established, became not a subject for criticism, however, but one of its most significant and important features, for it indicated the influence of factors previously considered as of little moment.

The regularity of the phenomenon under suitable conditions enabled us to determine many of the laws which govern it. In many cases these suitable conditions were sufficiently persistent to ensure the repetition of the phenomenon week after week, and even month after month. Also the conditions of experiments undertaken in the laboratory by eight or nine experimenters over many years were sufficiently varied to show the general nature of the phenomenon. [Probably not more than 1/20th part of the experimental evidence has been recorded.]

In an attempt to obtain more complete control, it was, of course, essential to use a Coolidge tube. Such tubes had previously been employed, but not under the best conditions. In Dunbar's experiments[†], for instance, in which an induction coil and mercury interrupter were used, the discontinuities certainly appeared, but the conditions were not sufficiently controllable, nor was the experiment itself of the kind which was later found most suitable to exhibit the phenomenon.

In other experiments with the Coolidge tube (conducted by Mr. Stevens: results unpublished) extensive series of observations showed the very precise difference in the levels of activity of a primary and of a scattered beam, exactly as with gas tubes away from the region of a discontinuity, showing that the same laws were operative with the Coolidge and gas tubes. But on only one occasion was there observed the change of activity in one beam such as characterizes a J discontinuity. The tube in this case also was worked by an induction coil and mercury interrupter. The only partial success of the experiments with the Coolidge tube and induction coil with mercury interrupter led to our use of a rotary converter with transformer to supply the high potential.

---

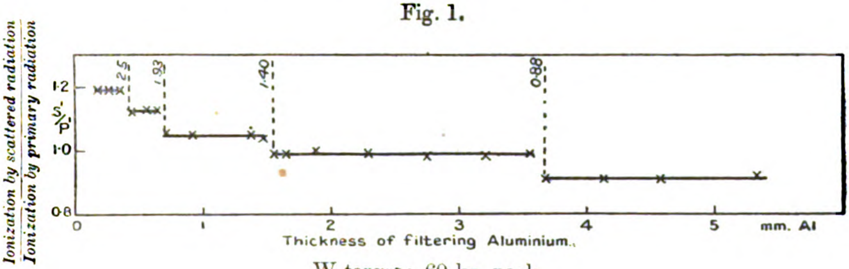
[*] Communicated by the Authors.

[†] Phil. Mag., January 1925.

By very careful regulation of the filament current in the Coolidge tube, and of the applied potential, some of the most interesting results have been obtained.

The experiment, in brief, was to compare the radiations scattered from a paraffin cylinder in the direction making an angle of 90° with the primary beam with the primary itself by the method of Barkla and Khastgir—*i. e.*, by placing successive equal thicknesses of aluminium in both beams and studying the ratio of the ionizations produced by these two in similar electroscopes. Typical results are shown in fig. 1, in which the ratio of ionizations by scattered and primary radiations is plotted against thickness of filtering aluminium placed in the path of each. The constancy of this ratio, $\frac{\text{ionization by scattered radiation}}{\text{ionization by primary radiation}}$, for various thicknesses of aluminium shows the precisely equal absorptions of scattered and primary radiations between the J discontinuities. The discontinuities show the sudden changes in the ionization produced by the scattered radiation when by filtering this arrived at certain critical absorbabilities, or at any rate at certain average constitutions measured to a first degree of approximation by an average absorption-coefficient. These, of course, are the J discontinuities similar to those observed by Barkla and Khastgir in a comparison of the scattered with the primary X-radiation, and by Barkla and Gladys I. Mackenzie in the radiation scattered at 120°, when compared with that scattered at 60° with the primary.

Fig. 1.



W target: 60 kv. peak.

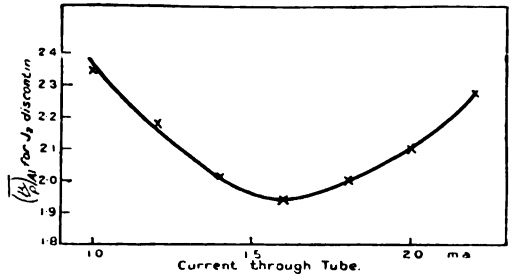
The important features of these experiments are the following :—

(1) By careful control it has been found possible to obtain consistent results throughout the whole series of experiments. The J discontinuities have been observed without exception in every experiment ; they appear to be under perfect control.

(2) New discontinuities have been observed between what have been previously called J_1 and J_2 and also between J_2 and J_3. The second of these had, however, been observed in one or two experiments by Miss Mackenzie. In our experiments it occurred without exception.

(3) In previous experiments the discontinuities had appeared at absorbabilities which, though calculated from a 50-per-cent. absorption, were remarkably constant. In these experiments a regular systematic variation of $\overline{\left(\frac{\mu}{\rho}\right)}_{Al}$ (calculated from a 50-per-cent. absorption) has been obtained by varying the current through the Coolidge tube. Thus fig. 2 shows the relation between $\overline{\frac{\mu}{\rho}}$ corresponding to the critical state for the J_2 discontinuities and the current through the tube in milliamperes. The critical absorbability, as previously measured, is thus appreciably dependent upon the total measure of the stream of electrons striking the anti-cathode. Such a dependence of the critical $\overline{\frac{\mu}{\rho}}$ upon the current passing through the tube has been found for each of the discontinuities observed.

Fig. 2.



Mo target: 40 kv. peak.

(4) Further, in each case a relationship of the form shown in fig. 2 for the J_2 discontinuities has been found. In each case also the minimum value for $\frac{\bar{\mu}}{\rho}$ corresponds very closely with the value which was found to be so constant in the experiments with gas-tubes and with a mercury break interrupter. In our experiments these minimum values of $\left(\frac{\bar{\mu}}{\rho}\right)_{\mathrm{Al}}$ are

3·76, 3·24, 2·44, 1·94, 1·40, 0·73, 0·47,

corresponding to the values—

J_1			J_2		J_3	J_4	J_5
3·8	—	—	1·9	—	0·7	(0·47)	0·34

previously published *.

That this variation in the critical value of $\frac{\bar{\mu}}{\rho}$ was not due simply to variation in intensity of the radiation was shown by experiments at different distances from the anti-cathode. When the current through the tube was constant, the critical absorbability was independent of distance from the tube, and thus of simple intensity. The variations illustrated in fig. 2 are thus not fundamentally associated with intensity of radiation; they are dependent on a quality of the whole stream of radiation generated at the anti-cathode.

It should, however, be pointed out that the method of measuring the absorbability of a complex radiation, by taking a 50-per-cent. diminution of the ionization, is a quite arbitrary one. And our method of measuring the average constitution could not be expected to give the quantity defining the position of a J discontinuity with any precision. The remarkable feature has been that it has varied so little under great variety of conditions. This is partially explained by the relationship illustrated in fig. 2, for the critical $\frac{\bar{\mu}}{\rho}$ as previously published is really a minimum value, so there is little variation of its value over a wide range of current.

With a given current through the tube, a variation of potential applied to the tube of course changed the wave-length and general absorbability; but the critical absorbability for the discontinuity was not appreciably changed.

---

* "The J Phenomenon (Part I.)," Phil. Mag., May 1925.

Thus, when a lower potential was applied, the radiation was of lower frequency, softer, and thus had to be filtered by greater thicknesses of aluminium before the critical absorbability was reached—in agreement with previous experiments.

The only difference observed between the absorbabilities of scattered and of primary radiations throughout these experiments has been in the appearance of the J discontinuities (or absorption lines) in the progressive absorption of the scattered radiation. Thus the horizontal lines between the discontinuities of fig. 1 show the precisely equal absorptions of secondary and primary. Such relationship as that of fig. 1 has previously been shown by Barkla and Miss Mackenzie for secondary radiations scattered at angles of 120° and 60°. Barkla and Khastgir, however, usually found that beyond the discontinuity the scattered radiation was more absorbable than the primary, although it was equally absorbable before the occurrence of the discontinuity; that is, the discontinuity initiated a definite change in the level of absorbability of the secondary radiation. In our experiments the difference between the secondary and primary was shown only at the discontinuities. There was never any evidence of a difference in absorbability provided the discontinuities did not become blurred by the variation of conditions during the experiment.

As the position of a discontinuity measured as indicated depends on the current through the tube, it would be expected that under variable conditions these discontinuities would be spread out and would show an apparently steady higher absorption of the scattered than of the primary radiation, such as has frequently been found in experiments on the progressive absorption of both beams. This suggests that all the apparent differences between scattered and primary radiations as shown by some absorption experiments may be fundamentally made up of such discontinuities.

There is, of course, a vast field for research in the subject of the J phenomenon. We wish for the present only to record the advances made in these experiments, a fuller account of which will appear elsewhere.

Summary.

Control of the J discontinuities and associated phenomena has been obtained.

Further discontinuities have been found.

The critical absorbabilities (as usually measured) have been found to vary systematically with the current through the Coolidge tube.

In these controlled experiments no difference has been observed between the absorptions of primary and scattered radiations, except by the occurrence of the J discontinuities (or absorption lines) in the progressive absorption of the scattered radiation.

CV. *The Density of Fluids.*—I. *On a Relation between Density and Temperature and on the Latent Heat of Vaporization.*

By J. H. SHAXBY, *D.Sc., F.Inst.P., Physiology Institute, Cardiff**.

THE average value of the intermolecular distances in any fluid, or in other words the density of the fluid, must obviously be determined by a sort of balance between molecular attractions tending to greater condensation and molecular movements tending to wider dispersal. The following paper is a somewhat speculative attempt to give these general notions a greater precision.

Just as the relation of density to height in the case of an isothermal atmosphere is given by the equation

$$\rho = \rho_0 e^{-\frac{V}{RT}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which ρ is the density at a height where the potential energy is V, and ρ_0 the density at datum level where the potential energy is zero, so we may suppose that the uniform density ρ of a fluid is given by an equation of the same form, where V now denotes the potential energy of intermolecular forces corresponding to the actual state of packing of the molecules, and ρ_0 is the density of close packing when this potential energy is zero. V is itself therefore a function of the density ρ, and the problem resolves itself into that of finding the form of that function.

To remove a molecule, initially in close proximity to a second, to an infinite distance in the absence of other molecules would require an amount of work E_0, and in falling back the same amount of work would be done by the molecule. In the case of an actual fluid this process becomes less simple: other molecules intervene and disturb the returning one by their attractive forces and by collisions. Hence when a molecule, coming from infinity, does at last reach the second or "goal" molecule it brings with it a quantity of energy which is no longer E_0. We may look at the matter in a rather different way by supposing the moving molecule to have reached a given stage in its journey, and considering its chances of continuing a stage further in the right direction without more than a permissible disturbance. Thus if a molecule P is at a given instant moving towards the "goal" molecule, its direction must lie within a cone of solid angle determined by the diameter of the molecules and its distance from its destination, the axis of the cone being the line joining the centres of the given molecules. Let us call the solid angle ω. The distribution of the remaining molecules may be supposed to possess a simplifying regularity, such that the molecules nearest P all lie on the surface of a sphere with its centre at P and of radius r equal to the average distance apart of molecules in the fluid of density ρ. The product ρr^3 is constant for any given fluid, so the area ωr^2 cut off on this spherical shell by the cone is inversely proportional to $\rho^{2/3}$, while the surface density of molecules in the shell is directly proportional to the same quantity. With closer packing, the chance of the molecule P coming within a given distance from another molecule is of course increased, but since all intermolecular distances are at the same time decreased P is moving, so to speak, in a "stiffer" field. The chance of a disturbance, measured by the angular deflexion of P's path, exceeding any specified amount is determined by the ratio of the distance of approach to the mean distance r. Thus for a given angular displacement the distance of approach must be reduced in the same proportion as r. So we may take as the measure of the disturbance the chance of the ratio of the distance of P from a second molecule on its passage through the shell to the distance r being less than some assigned value. This chance is proportional to the number of molecules of the shell in the area ωr^2 and is thus constant, whatever the packing.

---

* Communicated by the Author.

This is otherwise obvious, since the number of molecules in the shell remains constant as the density increases, so that the chance of a molecule lying within the solid angle ω also remains unchanged. The chance of a given angular disturbance of P's motion is thus independent of the density of the fluid.

In traversing any given distance x, P has to run the gauntlet of such disturbance x/r times, and the total chance of a given deviation is thus inversely proportional to r, in other words directly proportional to the cube root of the density. The chance of escaping such deviation is thus proportional to $1-c\rho^{1/3}$, where c is a constant.

Hence, with a large number of molecules such as P, the fraction which succeeds in bringing its quota of energy E_0 to the goal molecule is $1-c\rho^{1/3}$, so that the effective average energy is

$$E_0(1-c\rho^{1/3}) = E_0-B\rho^{1/3}.$$

We may conveniently deal with a gramme-molecule of the substance, so that the symbols E_0, R, etc. refer to that quantity, *i. e.*, to $6{\cdot}07\times 10^{23}$ molecules.

Thus, writing $B\rho_1{}^{1/3}$ for E_0 and $\alpha/3$ for R/B, we have

$$\rho = \rho_0 e^{-\frac{B(\rho_1{}^{1/3}-\rho^{1/3})}{RT}} = \rho_0 e^{-\frac{3(\rho_1{}^{1/3}-\rho^{1/3})}{\alpha T}} \quad . \quad . \quad (2)$$

Hence

$$\rho_1{}^{1/3}-\rho^{1/3} = \frac{\alpha T}{3}(\log_e\rho_0-\log_e\rho) = \alpha T(\log_e\rho_0{}^{1/3}-\log_e\rho^{1/3}), \quad (3)$$

or

$$\rho^{1/3}-\alpha T\log_e\rho^{1/3} = \rho_1{}^{1/3}-\alpha T\log_e\rho_0{}^{1/3}. \quad . \quad . \quad (4)$$

2. Applying these equations to a liquid and its saturated vapour both at absolute temperature T, and denoting their densities by ρ and σ respectively, we have

$$\rho^{1/3}-\sigma^{1/3} = \alpha T\log_e\left(\frac{\rho}{\sigma}\right)^{1/3}, \quad . \quad . \quad . \quad . \quad (5)$$

from which we can calculate the value of α. Table I. gives the result for a number of substances over wide ranges of temperature, the highest being in most cases the critical temperature. The data have been drawn from the values of ρ and σ given in the article on Vapour Pressures (L. Graetz) in Winkelmann's *Handbuch der Physik*, Kaye and Laby's Tables and *l'Annuaire du Bureau des Longitudes.*

The value of α at the critical temperature T_c is $\frac{\rho_c{}^{3}}{T_c}$, the limiting value of $\frac{\rho^{1/3}-\sigma^{1/3}}{T\log_e\left(\frac{\rho}{\sigma}\right)^{1/3}}$ when both ρ and σ become equal to the critical density ρ_c.

It will be seen that the value of α is nearly independent of temperature, at least for substances which are not associated in the liquid state. Values of ρ_0 and ρ_1 were determined by trial and the equation (4) above found to hold satisfactorily, but such methods of evaluating ρ_0 and ρ_1 are unnecessary, as will be shown, so their values are not inserted here.

TABLE I.

WATER.

Temp.° C.	$a \times 10^3$.
0	2·07
20	2·13
40	2·19
60	2·24
80	2·28
100	2·31
120	2·31
364·2 (Crit.)	2·50

MERCURY.

Temp.° C.	$a \times 10^3$.
180	2·88
220	2·91
260	2·94
300	2·95
340	2·95
360	2·95

CARBON DISULPHDE.

Temp.° C.	$a \times 10^3$.
−3·1	3·30
8·2	3·20
16·3	3·31
22·4	3·32
27·0	3·32
373 (Crit.)	3·05

AMMONIA.

Temp.° C.	$a \times 10^3$.
0	3·43
20	3·45
40	3·46
60	3·44
80	3·42
100	3·39
132·9 (Crit.)	3·51

CARBON DIOXIDE.

Temp.° C.	$a \times 10^3$.
0	5·75
10	5·75
30	5·82
30·5	5·83
31	5·84
31·35 (Crit.)	5·86

ISOPENTANE.

Temp.° C.	$a \times 10^3$.
20	3·05
60	3·06
100	3·04
140	3·02
180	3·04
186	3·05
187·8 (Crit.)	3·08

ETHER.

Temp.° C.	$a \times 10^3$.
20	3·05
60	3·09
100	3·09
140	3·08
180	3·09
190	3·12
193·8 (Crit.)	3·16

PENTANE.

Temp.° C.	$a \times 10^3$.
40	2·96
80	2·96
120	2·95
160	2·95
180	2·95
190	2·97
197·2 (Crit.)	2·94

HEXANE.

Temp.° C.	$a \times 10^3$.
60	2·70
100	2·72
140	2·72
180	2·72
220	2·74
230	2·75
234·7 (Crit.)	2·80

The values of α in Table I. are thus found by assuming that equation (4) holds equally for liquid and vapour, and the constancy of the resulting figures shows that this assumption is approximately true. But it appears desirable to explore the equation further, which we may do by taking the value of α at the critical temperature where there is no distinction between liquid and vapour and inserting this value $\frac{\rho_c^{1/3}}{T_c}$ in equation (4). We thus have

$$\rho^{1/3} - \frac{\rho_c^{\frac{1}{3}}T}{T_c}\log_e \rho^{1/3} = \rho_1^{1/3} - \frac{\rho_c^{\frac{1}{3}}T}{T_c}\log_e \rho_0^{1/3}, \quad . \quad . \quad (6)$$

which at the critical temperature reduces to

$$\rho_c^{1/3}(1 - \log_e \rho_c^{1/3}) = \rho_1^{1/3} - \rho_c^{1/3}\log_e \rho_0^{1/3}. \quad . \quad . \quad (7)$$

Now at the critical temperature it is reasonable to suppose, as has often been done, that molecular kinetic and potential energies become equal. Thus $V_c = \frac{3}{2}RT_c$.
Hence from equation (1)

$$\frac{\rho_c}{\rho_0} = e^{-3/2},$$

or

$$\rho_0^{1/3} = e^{1/2}\rho_c^{1/3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Substituting this value in (7),

$$\rho_c^{1/3}(1 - \log_e \rho_c^{1/3}) = \rho_1^{1/3} - \rho_c^{1/3}(\tfrac{1}{2} + \log_e \rho_c^{1/3})$$

or

$$\rho_1^{1/3} = \tfrac{3}{2}\rho_c^{1/3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We may thus rewrite equation (6) in the form

$$\rho^{1/3} - \frac{\rho_c^{\frac{1}{3}}T}{T_c}\log_e \rho^{1/3} = \tfrac{3}{2}\rho_c^{1/3} - \frac{\rho_c^{\frac{1}{3}}T}{T_c}\log_e (e^{1/2}\rho_c^{1/3}),$$

i. e.

$$\frac{\rho^{1/3}}{\rho_c^{1/3}} - \frac{T}{T_c}\log\frac{\rho^{1/3}}{\rho_c^{1/3}} = \tfrac{3}{2} - \tfrac{1}{2}\frac{T}{T_c}. \quad . \quad . \quad . \quad (10)$$

If we put $\frac{\rho^{1/3}}{\rho_c^{1/3}} = \phi$ and $T/T_c = \theta$, we obtain a "reduced" equation, containing no quantities specific to any particular substance:

$$\phi - \theta\log_e \phi = \frac{3-\theta}{2}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Further, $V = E_0\left(1 - \frac{\rho^{1/3}}{\rho_1^{1/3}}\right)$, of which a special case is $V_c = E_0\left(1 - \frac{\rho_c^{1/3}}{\rho_1^{1/3}}\right)$. But $V_c = \frac{3}{2}RT_c$ and $\frac{\rho_c^{1/3}}{\rho_1^{1/3}} = \frac{2}{3}$.

Therefore $\quad \frac{3}{2}RT_c = \frac{1}{3}E_0$, or $E_0 = \frac{9}{2}RT_c$. . . . (12)

Hence the characteristic molecular energy E_0 of a substance is numerically equal to three times the kinetic energy at the critical temperature. The critical temperature may thus be taken as a measure of this characteristic energy, the energy required to dissipate the substance from a state of close molecular packing to one of infinite separation of its molecules. Numerically, E_0 is $3·74T_c \times 10^8$ ergs or approximately $9·T_c$ calories per gram-molecule, $6·17T_c \times 10^{-16}$ erg per single molecule.

3. The values of $\rho_0^{1/3}$, $\rho_1^{1/3}$, E_0, and V_c, estimated from the experimental data for densities at different temperatures, are shown in Table II. together with the corresponding quantities $e^{1/2}\rho_c^{1/3}$, $\frac{3}{2}\rho_c^{1/3}$, $\frac{9}{2}RT_c$, and $\frac{3}{2}RT_c$, for a number of substances.

TABLE II.

Substance.	$\rho_0^{1/3}$.	$e^{1/2}\rho_c^{1/3}$.	$\rho_1^{1/3}$.	$\frac{3}{2}\rho_c^{1/3}$.	$\frac{\rho_0^{1/3}}{\rho_1^{1/3}}$.
Water	1·142	1·139	1·039	1·036	1·099
Mercury	2·692	—	2·447	—	1·091
Carbon disulphide ...	1·215	1·191	1·128	1·084	1·077
Ammonia	1·055	1·020	0·941	0·927	1·120
Ether	1·065	1·055	0·962	0·960	1·107
Isopentane	1·000	1·016	0·910	0·925	1·099
Heptane	1·038	1·016	0·931	0·925	1·114
Methyl propionate ...	1·135	1·119	1·022	1·018	1·111
Diisopropyl	1·001	1·010	0·920	0·932	1·088

	10^{10} ergs/gm. molec.			
Substance.	E_0.	$\frac{9}{2}RT_c$.	V_c.	$\frac{3}{2}RT_c$.
Water	23·52	23·85	7·89	7·95
Mercury	—	—	—	—
Carbon disulphide...	19·06	20·43	6·85	6·81
Ammonia	15·40	15·19	5·28	5·06
Ether	17·20	17·47	5·75	5·82
Isopentane	17·18	17·24	5·46	5·75
Heptane	20·99	20·21	7·06	6·74
Methyl propionate...	20·46	19·85	6·78	6·62
Diisopropyl	18·17	18·73	5·90	6·24

The ratio of $\rho_0^{1/3}$ to $\rho_1^{1/3}$ is also given; as shown above this ratio should be $\frac{e^{1/2}}{3/2}$ or 1·099.

Table III. exhibits the general fit of equations (4) or (6). Examination of this table shows that the equations hold with a high degree of accuracy for liquids, but less closely for saturated vapours. The latter give a fair approximation at temperatures not too far from the critical, *i.e.* when the vapour density is great, but there are increasing divergences as the temperature falls.

TABLE III.

Temp.° C.	$\rho_1^{1/3} - a\mathrm{T}\log\rho_0^{1/3}$.	$\rho^{1/3} - a\mathrm{T}\log\rho^{1/3}$.	$\sigma^{1/3} - a\mathrm{T}\log\sigma^{1/3}$.
WATER ($a = 2{\cdot}496\times10^{-3}$, $\rho_1^{1/3} = 1{\cdot}039$, $\rho_0^{1/3} = 1{\cdot}142$).			
0	1·000	1·000	
60	0·992	0·996	
120	0·982	0·989	
364·3............	0·947	0·946	
AMMONIA ($a = 3{\cdot}508\times10^{-3}$, $\rho_1^{1/3} = 0{\cdot}93$, $\rho_0^{1/3} = 1{\cdot}02$).			
0	0·9218	0·9234	1·008
40	0·9206	0·9207	0·9297
80	0·9194	0·9198	0·9322
132·9............	0·9177	0·9158	
HEPTANE ($a = 2{\cdot}60\times10^{-3}$, $\rho_1^{1/3} = 0{\cdot}925$, $\rho_0^{1/3} = 1{\cdot}016$).			
80	0·9182	0·9189	0·9523
120	0·9175	0·9176	0·9378
160	0·9167	0·9165	0·9309
200	0·9159	0·9163	0·9282
240	0·9153	0·9161	0·9224
260	0·9148	0·9149	0·9164
264	0·9147	0·9142	0·9144
266·9	0·9147	0·9184	

TABLE IV.

(ϕ_1 liquid, ϕ_2 saturated vapour.)

Temp.	θ.	ϕ_1.	ϕ_2.	$\phi_1 - \theta\log_e\phi_1$.	$\phi_2 - \theta\log_e\phi_2$.	$\frac{3-\theta}{2}$.
HEPTANE.						
80......	0·654	1·391	0·204	1·175	1·243	1·173
140......	0·765	1·346	0·347	1·119	1·157	1·118
180......	0·839	1·307	0·457	1·083	1·114	1·081
220......	0·913	1·253	0·593	1·047	1·070	1·044
250......	0·969	1·182	0·739	1·020	1·032	1·016
METHYL PROPIONATE.						
80......	0·666	1·391	0·217	1·171	1·234	1·167
180......	0·854	1·299	0·485	1·076	1·103	1·073
255......	0·996	1·100	0·879	1·005	1·007	1·002

The "reduced" equation (11) is tested in Table IV., which shows the same imperfect agreement for vapours and good fit for liquids.

4. The relations obtained above give a means of calculating the critical temperature and critical density of substances for which these data have not been found by direct measurement.

For instance, equation (11) may be rewritten in the form

$$\tfrac{3}{2}\psi - \theta \log_e \tfrac{3}{2}\psi = \frac{3-\theta}{2}, \text{ if we write } \psi \text{ for } \frac{\rho^{1/3}}{\rho_1^{1/3}}.$$

This reduces, for calculation, to

$$T_c = \frac{0\cdot0630 - 1\cdot535 \log \psi}{1-\psi} T.$$

It is found that for saturated vapours the quantity ρ_0 must be replaced by successively smaller values as one goes from higher to lower temperatures in order to force a fit with equation (4). At the lowest temperatures good agreement is found if one replaces ρ_0 by ρ_1. Using this purely empirical fact, we have for vapours of low densities the relation

$$T_c = -\frac{2 \log_e \psi}{3(1-\psi)} T. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Thus, applying (13) to liquid mercury at 260° C., $\psi = 0\cdot960$, taking $\rho_1^{1/3}$ as 2·447 (Table II.). The calculated value of T_c is 1209° Abs. or 936° C. From the data for 360° C. we find 1032° C. for T_c.

Using (14) for mercury vapour at 180°, 220°, and 260° C., we find respectively 998°, 981°, and 972° C. as the critical temperature.

Again we may evaluate this temperature from the relation $\alpha = \frac{\rho_c^{1/3}}{T_c} = \frac{2\rho_1^{1/3}}{3T_c}$. For mercury α is $1\cdot28 \times 10^{-3}$, whence T_c is 996° C.

These estimates then agree in suggesting that the critical temperature of mercury is about 980° C. and its critical density about 4·35. Assuming the quantity $\frac{RT\rho}{p}$ at the critical temperature to be of its usual order of magnitude, the critical pressure indicated is about 600 atmospheres.

5. We may then conclude that the density of a fluid is represented by an expression of the form $\rho = \rho_0 e^{-\frac{V}{RT}}$, where the energy term $V = E_0 - B\rho^{1/3}$. E_0 is characteristic of each substance and is independent of the temperature and state of aggregation. The difference between V_1, the value for the liquid form at any temperature T, and V_2, the value for the saturated vapour at the same temperature, represents the difference between the amounts of work done when the molecules are dissipated beyond each others' range of attraction, according as we start with the liquid or the vapour phase. We should accordingly expect the work $V_2 - V_1$ to be intimately related to the internal latent heat o vaporization at the temperature T. Now $V_2 - V_1 = RT \log_e \rho/\sigma$, from (1), and it is well known that the internal latent heat of vaporization is represented with considerable accuracy by the expression $CRT \log_e \rho/\sigma$, where C is a number, approximately 1·7 to 2, varying somewhat for different substances, and rising slowly with temperature near the critical point to the latter figure, 2.

Further, Mills has shown that the internal latent heat is also given with some accuracy by an expression of the form $K(\rho^{1/3} - \sigma^{1/3})$, where K is constant for a given substance. Mills derived this expression on the assumption that the law of attraction between molecules is that of the inverse square. From considerations of surface tension and many other properties of liquids we know that such a law of force is impossible, and Mills's work has consequently been strongly criticised and has perhaps not received the attention it deserves. From equation (5) we see that if the internal latent heat is equal to $CRT \log_e \rho/\sigma$, it must also be given by Mills's expression. The latter results, in fact, not from any particular form of the law of intermolecular force, but from purely kinetic considerations, as set forth in the first section above.

6. The "maximum density" ρ_0 is given by equation (8) above in terms of the critical density. From ρ_0 we may calculate the diameter of a molecule of the substance. A few values are given in the first column of Table V.; the two other columns give the values drawn from measurements of viscosity, (*a*) by the usual equations, (*b*) as given by Sutherland. These data are quoted from Kaye and Laby's Tables.

A large number of molecular diameters have been calculated in this way and the data obtained will be discussed in a further paper.

TABLE V.

Molecular Diameters.

Substance.	From $\rho_0 = e^{3/2}\rho_c$.	From Viscosity Measurements.	
		(*a*)	(*b*) Sutherland.
Hydrogen	2·88	2·47	2·17
Helium	2·82	2·18	1·92
Argon..................	3·03	3·36	2·66
Nitrogen	3·21	3·50	2·95
Oxygen	3·01	3·39	2·71
Nitrous Oxide	3·30	4·27	3·33
Carbon Monoxide...	3·21	3·50	2·74
Carbon Dioxide ...	3·27	4·18	2·90

Summary.

It is shown that the density ρ of a fluid can be represented by the equation

$$\rho^{1/3} - \alpha T \log \rho^{1/3} = \rho_1^{1/3} - \alpha T \log \rho_0^{1/3},$$

where ρ_0 is the "maximum" density of the substance, and ρ_1 and α are constants. Further $\alpha = \rho_c^{1/3}/T_c$, where the subscript denotes data at the critical temperature.

It is shown that $\rho_1^{1/3} = \frac{3}{2}\rho_c^{1/3}$ and $\rho_0^{1/3} = e^{1/2}\rho_c^{1/3}$. A "reduced" equation containing no constants peculiar to a particular substance is also obtained. These equations hold very closely for liquids, approximately for saturated vapours.

The internal latent heat of vaporization L_i is discussed and it is shown that Mills's Equation $L_i = K(\rho^{1/3} - \sigma^{1/3})$ ($\rho =$ density of liquid, $\sigma =$ that of vapour) can be deduced from kinetic considerations and does not depend as he supposed upon an inverse square law for intermolecular attractions.

From the "maximum" density ρ_0 the diameters of molecules can be estimated.

CVI. *On a Simple Light-Quantum.*

By Prof. E. T. Whittaker, *F.R.S.**

THE light-quantum described below is a solution of the ordinary Maxwell's equations of the electromagnetic field, and therefore behaves in accordance with the "classical" theory so far as refraction, interference, polarization, etc., are concerned. But it has the property, which is required for "quantum" phenomena, that if, after it has travelled any distance, however great, from its source, it encounters an atom, then the atom will in certain cases absorb *the whole* of the energy of the light-quantum, even though that energy was, immediately before the encounter, distributed over a very large region of space.

Consider first an ordinary elementary magnetic molecule at a point O, whose axis is in the line AB. We shall for the moment regard this in the old-fashioned way as the limit of a positive magnetic charge m at the point B, together with a negative magnetic charge $-m$ at the point A. This molecule sets up a magnetic field extending over all space.

The ordinary law of action of magnetic charges asserts that the charges at A and B attract each other, so they must be supposed to be kept apart by some arrangement in the material molecule in which they are embedded.

Now, let Ox be a direction at right angles to AB, and suppose that the magnetic molecule is set in motion in the direction Ox. Since a moving magnet generates an electric field which can act on another moving magnet, the force between the charges A and B is now affected by this additional force, which diminishes the original force between them. As the velocity of the magnetic molecule along Ox increases, the total force between the two charges continually decreases, until in the limit when the molecule is moving with the velocity of light, the force is exactly null: the electromagnetic force due to the motion exactly neutralizes the purely magnetic force. Thus if the molecule is moving with the velocity of light, we have no longer any need of the material framework to keep the two charges apart, and we can suppose the charges completely disembodied.

---

* Communicated by the Author.

Now consider what has happened to the field. As was shown long ago by Heaviside, when the molecule is set in motion in the direction Ox, the lines of magnetic force due to the molecule tend to draw in nearer to the molecule so far as the direction Ox is concerned, so that they concentrate towards the plane through O perpendicular to Ox ; until in the limit, when the velocity of the molecule is the velocity of light, the lines of force are entirely confined to this plane (which, of course, is travelling with the velocity of light), the field in the rest of space being null. There will now be lines of electric force (due to the motion of the magnetic charges) as well as lines of magnetic force, and the lines of electric force will be everywhere perpendicular to the lines of magnetic force : in short, what we now have is essentially a plane wave of ordinary light. The original magnetostatic field has become a plane wave of light, by merely setting it in motion with the velocity of light.

This plane wave of light, however, will have two peculiarities which distinguish it from the plane wave of light of the ordinary text-books. In the first place, the intensity of the disturbance is not the same over the whole of the infinite plane wave-front, but diminishes as we go outwards from the centre O of the plane, and is null at infinity. This is a satisfactory feature, since Baldwin and Jeffery have shown recently * that the old-fashioned plane-wave, with its intensity the same all over its infinite front, is an impossibility in general relativity. In the second place, our wave has a singularity at the point O, representing, in fact, the disembodied form of the magnetic molecules with which we started. This singularity we shall call the "*speck*" on the wave-front.

As a matter of fact, if we take the axis of z along AOB, and take an axis of y at right angles to the axes of x and z, then the electric force (E_x, E_y, E_z) and the magnetic force (H_x, H_y, H_z) in the wave-front are given by the equations

$$E_x=0, \qquad E_y=\frac{\partial}{\partial z}\left(\frac{z}{y^2+z^2}\right), \qquad E_z=-\frac{\partial}{\partial y}\left(\frac{z}{y^2+z^2}\right),$$

$$H_x=0, \qquad H_y=-E_z, \qquad H_x=E_y,$$

and this field satisfies Maxwell's equations, except at the point ($y=0$, $z=0$), which is the "speck."

---

* Proc. Roy. Soc. cxi. p. 95 (1916).

It is the "speck" which confers on the wave the desired "quantum" properties, for in the original magnetostatic field, anyone who takes hold of the magnetic molecule and moves it about, thereby moves the whole of the magnetic field ; the magnetic field is, so to speak, led captive by the magnetic molecule. This property—that the whole field is an appanage of the magnetic molecule and can be carried about with it—still persists in the limiting case which we have considered, in which the magnetic molecule has shed its materiality and has become the "speck" on the wave-front of the light : it is still true that anyone who can take hold of and capture the "speck" thereby captures the whole of the energy in the light-wave, which is really a mere appanage of the "speck."

Now the "speck" retains the property possessed by the original magnetic molecule, of being acted on by magnetic forces (and, since it is in motion, by electric forces also) ; and therefore, if the "speck" happens to impinge on an atom, or to pass very near to one, there is a possibility that the speck may be attracted into the atom and swallowed up and, so to speak, digested by it. The result will be that *the whole* of the energy in the light-wave will now have become the property of the atom : it may be partly located in the space outside the atom, but it belongs to the atom in the sense that wherever the atom moves, this bundle of energy henceforth moves with it. Thus the theorem which Einstein many years ago deduced from thermodynamic reasoning, namely, that *every parcel of light-energy which is emitted from an atom is ultimately entirely absorbed by a single other atom* is here seen to be a consequence of the strict classical electromagnetic theory of light. If this fact has not been clearly perceived before, it is because the expounders of the classical theory have been led astray by that artificial and (as we now know) physically impossible creation of mathematical analysis, the infinite plane-wave of light.

October 4th, 1926.

CVII. *On the Rate and Mechanism of the Aeration of Water under Open-Air Conditions.* *By* W. E. ADENEY, *D.Sc., F.R.C.Sc.I., F.I.C.*[*]

THE problems of the rate at which the solution of oxygen and nitrogen occurs at the exposed surfaces of waters under open-air conditions, and of the mechanism by which the dissolved gases are transmitted to the unexposed portions of such waters, have become of considerable technical importance, especially in connexion with the disposal of normal sewage liquors by dilution with clean river waters, as recommended by the Royal Commission on Sewage Disposal in its eighth Report (1912), and also in connexion with the economical operation of the Bio-Aeration method of sewage purification.

A large number of experiments have been made in connexion with these problems—first by the writer (1), then by him in collaboration with the late Mr. H. G. Becker (2), and latterly by him in collaboration with Dr. A. G. G. Leonard and Miss A. Richardson (3).

Solution of Gases by Well-Mixed Water in Thin Films.

Adeney and Becker employed a method for determining the rates of solution of oxygen and nitrogen from the air by water, every part of which is successively exposed in thin films, and becomes aerated independently of downward "streaming."

The method consists of enclosing a large bubble of air of known volume in a long narrow tube containing de-aerated water, also of known volume, and of allowing the bubble to ascend through the water column repeatedly until saturation of the water by air has been reached, the water-air surface remaining unbroken throughout the experiment.

The time taken by the bubble to ascend the tube was measured in every case, and found to be practically constant, at 18 seconds per double journey.

The loss of pressure in the bubble of air was measured, after each double passage up the tube, by means of a water manometer, and afforded the necessary data for calculating the amount of gas dissolved, step by step, until saturation was reached.

The air in the bubble was renewed after each observation, by taking out the stopper of the tube and inserting into the air-space a tube connected with a filter-pump, which drew a current of air through the space.

---

[*] From the Scientific Proceedings of the Royal Dublin Society for April 1926. Communicated by the Author.

As the bubble of air ascends the tube from the bottom, the whole of the water gradually and uniformly flows over it in thin films, the mass of the water forming the films becoming mechanically and intimately mixed, after exposure of their surfaces to the air in the bubble, with the result that the column of water, when the experiment is properly carried out, becomes gradually charged with small additions of air throughout its length, by repeated passages of the bubble along the tube, until saturation is reached. So that the air-content of the column of water is uniform throughout its length at any intermediate stage of solution up to saturation. Bubbles of air of 5, 7·5, 10, 12·5, and 15 c.c. in volume were employed.

In the case of the bubble of 15 c.c. in volume, the thickness of the film was found to be 0·05 cm., and its effective area 71·33 sq. cm.

The solution of oxygen and nitrogen was found to take place in accordance with the formula

$$w = w_1 - (w_1 - w_0)\, e^{-f \frac{a}{v} t}$$

in which w = concentration at the end of t seconds.
w_1 = saturation concentration at the given temperature and pressure.
w_0 = initial concentration at start, when $t=0$.
f = coefficient of escape of the gas from the water per unit area.
v = volume of water.
a = area of surface exposed.

The coefficient f varies with temperature according to the equations

Oxygen $f = 0{\cdot}0096\,(T-237)$ per second.
Nitrogen $f = 0{\cdot}0103\,(T-240)$ „ „
Air $f = 0{\cdot}0099\,(T-239)$ „ „

It is noteworthy that, when the rates of solution are expressed in percentages of saturation, the curves drawn from the percentages of saturation for the three gases lie very close to each other, those for oxygen and nitrogen (pure) being practically identical.

It is possible to calculate, with the aid of this formula, the rate of solution of oxygen or nitrogen from the air, by films of fresh or salt waters, under different conditions of area of film and total volume of water, or initial degree of saturation, provided that the calculations are based upon data derived from experiments carried out so that all of the water is successively exposed in thin films, and thorough mixing is thus ensured.

From the results of the experiments described in the papers, Nos. 31 and 44 (2), and with the aid of the above formula, the rate of solution of oxygen from the air by films of fresh and of sea water, 0·05 cm. thick, have been calculated for temperatures between 0° C. and 30° C. The values obtained are given in Table I.

TABLE I.

Rates of Solution of Oxygen, expressed in Percentages of Saturation, by Films of De-aerated, Fresh, or Salt, Waters, 0·05 cm. thick, when uniformly exposed to the Air, *and independent of Evaporation and downward "Streaming."*

Temperature	0°	5°	10°	15°	20°	25°	30° C.
Percentage of saturation	Time in seconds.						
10 ...	1·0	0·8	0·8	0·7	0·7	0·6	0·5
20 ...	2·1	1·8	1·6	1·4	1·3	1·3	1·2
30 ...	3·2	2·7	2·3	2·0	1·8	1·7	1·6
40 ...	4·5	4·0	3·6	3·3	2·9	2·7	2·4
50 ...	6·0	5·2	4·6	4·2	3·9	3·6	3·3
60 ...	8·0	7·2	6·4	5·7	5·0	4·6	4·3
70 ...	10·5	9·3	8·2	7·3	6·7	6·1	5·8
80 ...	14·0	12·5	11·0	10·0	9·0	8·3	7·7
90 ...	19·8	17·5	15·6	14·2	13·0	11·9	10·8
99 ...	39·6	35·0	31·2	28·4	26·0	23·8	21·6

Pressure, 760 mm. (moist).

For practical purposes these values may be taken as approximately representing the maximum rates of solution of oxygen from the air by the exposed surfaces of water exposed to open-air conditions, at the given temperatures, independently of evaporation and downward "streaming."

Solution of Gases by Quiescent Columns of Water.

In the case of quiescent columns of de-aerated water, freely exposed to the air, the dissolved atmospheric gases do not remain concentrated at the surface film. The latter, on the contrary, as the gases are dissolved by it, sinks towards the bottom of the column, for the reasons given below, with the result that the column becomes aerated gradually, and more or less uniformly, from top to bottom during every step of the process of aeration, until completely aerated. At no time does the surface layer of a column of de-aerated water become saturated until the whole column of water throughout its depth is also nearly saturated.

From the results of the writer's experiments with three- and six-foot columns of water, and from those of the experiments recently carried out with great care in collaboration with Dr. A. G. G. Leonard and Miss Richardson with ten-foot columns of distilled water and of solutions of sodium chloride of various concentrations, it has been established that the aeration of quiescent columns of de-aerated water, both fresh and salt, under open-air conditions, is to be ascribed largely, though possibly not wholly, to the effects of evaporation from the exposed surfaces of the water.

Apparently, as evaporation proceeds from the surface of a body of quiescent water, the density of the exposed surface film of water is increased relatively to that of the unexposed portions of the water as a result of cooling, and also, in the case of salt waters, of concentration of the salts in solution, and the denser water sinks in minute imperceptible streamlets towards the bottom. The continuous downward "streaming" thus produced causes a corresponding upward displacement of unexposed portions of the water, and sets up an imperceptible, but efficient, process of mechanical mixing of the aerated surface film with the unexposed portions of the water. Although the mass of the water "streaming" downward from the exposed surface at any particular time must be relatively minute, it passes vertically downwards through the mass of water below the surface towards the bottom, and sets up a very efficient process of mixing, especially in the case of salt water. And since the experiments referred to above prove that the downward "streaming" is effective in causing as uniform mechanical mixing to depths of 10 feet as to 1, 3, and 5 feet, it may safely be assumed that it is effective in producing a similarly uniform mixing down to much greater depths.

The "streaming" sets up a more rapid and uniform process of mixing in salt waters than in fresh waters when the conditions obtaining over their exposed surfaces are favourable for free evaporation, owing, no doubt, largely, if not wholly, to the fact that in addition to the cooling effect of evaporation at the exposed surface film, there is also that of concentration of the salts in solution in the case of the former class of waters.

It may be noted, furthermore, that the process of "streaming" also proceeds more rapidly and uniformly at temperatures at and above 10° C. than below it in both fresh and salt waters. This is to be expected from the slow rate of evaporation at the lower temperatures, and from the fact of fresh water attaining its maximum density at 4° C.

It also depends upon the concentration of the salts in solution. The optimum concentration is equivalent to about 1·5 per cent. sodium chloride.

It may finally be concluded that there are five conditions upon which the mechanism of the aeration of fresh and salt waters, under open-air conditions, primarily depends. They are :—

(1) The area of water exposed to the air ;

(2) temperature ;

(3) humidity of the air ;

(4) salinity (in the case of tidal waters) ;

(5) wind, causing both an increase in area exposed and an acceleration of evaporation per unit area.

The influence of the humidity of the air and of the salinity of the water upon the rate of "streaming," and therefore upon the rate of mixing of the exposed with the unexposed portions of a water, has recently been quite independently confirmed by Dr. J. A. N. Friend's interesting and important experiments on the corrosion of iron (4).

The area of open waters exposed, in common with the other conditions, will not remain constant, but will be liable to considerable variation, according to the force of the wind or of water currents, or of both.

The turbulent action of these two factors will also effect a more or less rapid increase in the rate of solution of atmospheric gases by the exposed surface films of the water.

The formula applicable to the calculation of the rate of aeration of wholly or partly de-aerated quiescent columns of fresh and of sea waters, when their exposed surfaces are undisturbed, and the humidity and temperature of the air are uniform, is of the same form as that above given for the rate of solution of oxygen and nitrogen by thin films of water, when independent of evaporation and downward "streaming" (2, xvi. 13).

The effect of the humidity of the air in contact with the water on the rate of aeration is shown by the following experiment:—

Four tubes, each 320 mm. long and 40 mm. diameter, were placed in a thermostat after being filled with de-aerated water. The upper ends of three of these tubes, after 50 c.c. water had been withdrawn from each, were connected in series by means of rubber corks and glass tubing, so that a current of air could be drawn through the air-spaces. The fourth tube was left open to the atmosphere.

Unfiltered air was drawn through the air-space of tube 1, then through two U-tubes containing calcium chloride, and thence into the air-space of tube 2, whence it passed directly into the air-space of tube 3. Thus the air was much drier when passing through the air-space of tube 2 than when passing through the air-space of tube 1; while the air on being drawn through the air-space in tube 3 was nearly, if not wholly, saturated with aqueous vapour.

Tube 4 was exposed to the open air in the middle of the thermostat, where the humidity of the air was considerable.

The results obtained from this experiment are given in Table II.

TABLE II.

Experiment showing the Effect of the Humidity of the Air on the Rate of Aeration of Quiescent Columns of Distilled Water. Temperature, 15° C.

No. of tube.	Depth of water.	Degree of aeration in p.c. of saturation*.	Value of f_1.	Time of Exposure.	
				Actual.	Calculated from rate of solution at surface at 15° C. (Table I.)
	cms.		per hour.	hours.	minutes.
1	27·07	41·5	0·34	43·0	22·8
2	26·37	63·2	0·61	44·0	46·9
3	26·69	31·3	0·23	44·5	10·9
4	30·20	32·7	0·29	42·0	13·6

* Initial aeration of each column = 10·3 per cent. saturation.

Area of surface of column 1=12·56 sq. cm., of each of the other columns =12·25 sq. cm.

f_1=coefficient of escape per unit area.

On examining these results it will be noticed that the column exposed to the dried air absorbed more than twice as much air as the column exposed to the moist air.

It may be noted, in connexion with the above experiment, that the values of f_1 in other experiments with quiescent columns of fresh, and of sea waters, when exposed to fresh air and kept at as uniform a temperature as possible, were found to be equal to 0·388 and 0·509 respectively.

The figures in the last column of the above table give the times in which the columns would have been aerated to the percentages of saturation which they respectively attained under the conditions of the experiment, had the aeration of each column proceeded at the rate given in Table I. for surface films ·05 cm. thick, at 15° C.; that is, at the approximately maximum rate of solution of oxygen from the air by fresh and salt waters, as found by the bubble method for the same temperature.

On comparing these figures with the actual times of exposure given in the table, it appears that the rates of aeration of quiescent columns of water by "streaming," under the specified conditions, were about 113, 56, 245, and 185 times slower than the initial rate of solution by the surface film, ·05 cm. thick, according to the humidity of the air passing over their exposed surfaces.

These rates of aeration apply only in cases of experiments with water columns in the laboratory, in which the surface layers can be preserved undisturbed without difficulty.

Under natural conditions, however, the exposed surface of open water is usually in a more or less disturbed condition, and then the aeration by "streaming" becomes greatly accelerated, as shown by the following experiment, in which the exposed surfaces of quiescent columns of de-aerated fresh and sea waters were kept in a continuous state of gentle disturbance. In this experiment two tubes, each 110 cm. long and 5 cm. diameter, were nearly filled, one with de-aerated fresh water, and the other with de-aerated sea water. A fine glass rod stirrer, bent into the shape of a gridiron, 4 cm. broad, was fixed so that its lower end dipped 2·5 cm. below the surface of the water in each tube, and was mechanically rotated slowly for 19 hours, the speed being such that the surface was only moderately ruffled. At the end of this time the stirrers were stopped, and samples were drawn from the top and bottom layers of the water column in each tube, and the dissolved nitrogen content was determined with the following results :—

TABLE 3.

	Sea water.		Fresh water.		
	Top layer.	Bottom layer.	Top layer.	Bottom layer.	
At commencement ...	10·7	10·7	9·2	9·2	per cent. saturation.
19 hours later ...	98·3	96·5	80·4	73·4	per cent. saturation.

Temperature of each column, 8·3° C.

It is evident from the above results that, when the surface of the water is kept continuously and gently disturbed, the effective area exposed to the air becomes so much increased that the downward "streaming" is greatly augmented, with a corresponding acceleration of the rate of aeration of the whole column. And this is true when the experiment is carried out at the low temperature of 8·3° C. The results recorded in the table show that in the course of 19 hours the average aeration of the sea- and fresh-water columns was increased, on an average, from 10·7 and 9·2 to 97·4 and 76·9 per cent. saturation respectively.

These columns would have reached like degrees of partial aeration in approximately 13 and 5·5 hours respectively had their exposed surfaces remained undisturbed, and had the aeration of the columns proceeded at the initial rates of solution of oxygen as found by the bubble experiments.

It may, therefore, be fairly assumed that the minimum rates of aeration of open waters by "streaming" may be approximately twofold and fourfold slower respectively than the rate that would be found by calculation for the given depth from the results of the bubble experiments.

These rates of aeration for open waters may fairly be regarded as minimum rates, since the temperature at which the experiment was carried out was below 10° C., and since the air immediately above the columns of water must have been well charged with aqueous vapour during the experiment, owing to the fact that their surfaces were exposed to air partially enclosed within the mouths of the tubes containing the water.

In the Bio-aeration method of purification the sewage liquid is intimately mixed, while in the aeration tank, by blowing air through it from the bottom of the tank, or by a propeller partially submerged in it. Whichever means of mixing is adopted, the surface of the sewage liquid is kept in a state of turbulent agitation, and it will probably be found on investigation that the minimum rate of aeration of the sewage liquid by downward "streaming" will be fully equal to, or, owing to the greatly increased surface area, may even exceed, that found by calculation from the results obtained by the bubble experiments for the given depth of the liquid, assuming an effective absorbing area equal to the undisturbed surface area of the tank.

The author desires to express his indebtedness to Dr. H. H. Poole, Editor of the Scientific Proceedings of the Royal Dublin Society, for valuable suggestions given in the preparation of this communication for publication.

References.

(1) Adeney.—"Unrecognized Factors in the Transmission of Gases through Water." Sci. Trans. Roy. Dub. Soc. 1905, viii. 13, p. 161; also Phil. Mag. 1905, ix. p 630. See also supplementary volume vi. to the 5th Report of the Royal Commission on Sewage Disposal, 1908, Cd. 4284, p. 56.

(2) Adeney and Becker.—"On the Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water." Sci. Proc. Roy. Dub. Soc. 1918, xv. 31, p. 385; 1919, xv. 44, p. 609; 1920, xvi. 13, p. 143; also Phil. Mag. 1919, xxxviii. p. 317; 1920, xxxix. p. 385, and 1921, xlii. p. 87.

(3) Adeney, Leonard, and Richardson.—"On the Aeration of Quiescent Columns of Distilled Water and of Solutions of Sodium Chloride." Sci, Proc. Roy. Dub. Soc. 1922, xvii. 3, p. 19; also Phil. Mag. 1923, xlv. p. 837.

(4) Friend.—"The Corrosion of Iron in Water and in Neutral Salt Solutions." J. C. S. 1923, cxxiii. p. 2996.

CVIII. *On an Apparent Relation between the Rate in the Change of the Electric Resistance at Fusion and the Crystal Lattice of Metallic Elements. By* HARALD PERLITZ, *Assistant Professor of Theoretical Physics, University of Tartu* *.

1. THE electric resistance of metallic elements changes abruptly at fusion in such a way that the phase with the smaller specific volume has the smaller resistance †. The structure of metallic elements also suffers a sudden change at fusion, and as melting means a complete collapse

---

* Read at a meeting of the Naturalists' Society at Tartu, March 18, 1926. Communicated by the Author.

† P. W. Bridgman, Phys. Rev. (2) xvii. p. 61 (1921).

of the systematically arranged crystal lattices formed by the atoms of metallic elements in the solid state, in the place of which there appears a chaotic distribution in the liquid state, it is natural to look for a relation between the discontinuity of the electric resistance at fusion and the crystalline lattice of metallic elements. For this purpose the following table was compiled:—

TABLE.

Element.	Type of lattice[1].	Rate of change in resistance at fusion[2].	Mean rate.	Group-value.
Bismuth	Rhombohedral hexagonal.	·465[5]; ·467(5)[5]; ·476(5)[5]; ·47; 1/2[6]; ·43; ·45; ·45	·48	1/2
Gallium	Not determined.	·48[5]; ·58	·53	
Antimony......	Rhombohedral hexagonal.	·70; 67[7]	·69	
Sodium.........	Body-centred cubic.	1·37[5]; 1·34; 1·6[8]; 1·45; 1·44; 1·53[9]	1·45	3/2
Lithium	Body-centred cubic.	2·51[10]; 1·68; 1·27[9]	1·48[12]	
Potassium ...	Body-centred cubic.	1·44[5]; 1·39; 1·5[8]; 1·56; 1·53; 1·60[9]	1·50	
Rubidium.......	Not determined.	1·81[11]; 1·58[5]; 1·5[8]	1·54[13]	
Aluminium ...	Face-centred cubic.	1·65	1·65	
Cæsium	Not determined.	1·7[5]; 1·65; 1·7[8]; 1·79[9]	1·71	
Silver	Face-centred cubic.	1·98; 1·74	1·86	2
Cadmium......	Hexagonal close-packed.	1·8[5]; 1·96[5]; 1·97	1·91	
Lead............	Face-centred cubic.	1·9[5]; 1·95[5]; 2·06	1·97	
Thallium	Uncertain[3]	2·0[5]	2·0	
Copper.........	Face-centred cubic.	2·09; 1·97	2·03	
Zinc	Hexagonal close-packed.	2·0; 2·09	2·05	
Tellurium......	Rhombohedral[4].	2·1[5]	2·1	
Tin (rhombic).	Not determined.	2·10; 2·2[5] 2·21[5]; 2·12; 2·02	2·13	
Gold............	Face-centred cubic.	2·28	2·28	
Mercury	Tetrahedral hexagonal.	4·1; 4·09; 4·05; 4·90; 5; 3·21	4·23	4 (?)

---

[1] Authority, if not stated otherwise, Landolt-Börnstein, *Phys. chem. Tabellen*, pp. 865-867 (1923).

[2] Authority, if not stated otherwise, Landolt-Börnstein, *Phys. chem. Tabellen*, pp. 1051-1052 (1923).

[3] Karl Becker & Fritz Ebert, *ZS. f. Physik*, xvi. p. 169 (1923); *Phys. Ber.* vi. p. 21 (1925).

[4] A. J. Bradley, Phil. Mag. (6) xlviii. p. 490 (1924).

[5] Ernst Wagner, *Ann. Physik* (4) xxxiii. p. 1486 (1910).

[6] A. Guntz & W. Proniewski, *J. d. Chem. phys.* vii. p. 481 (1909).

2. Referring to the table, it should be mentioned that the change of resistance has hitherto been measured for 19 metallic elements, *i. e.* for roughly one-third of all metallic elements; for 16 of them the crystal lattices have been determined. These data, gathered from the literature on the subject, have been collected in the above table, where the elements are arranged according to their average change of resistance. The crystal lattices given in the 2nd column are data obtained from X ray analysis

3. The 3rd column contains all available data for the rate of change of resistance at fusion, which in each horizontal line are arranged in chronological order. From these have been computed the average values given in the 4th column. In computing the averages all data in the 3rd column were taken into account, except in two cases, as stated in footnotes 10 and 11; questionable is the average for mercury, because the data for it exhibit too much variation.

4. If the supposition is correct that there exists a definite relation between the rate of change of the electric resistance at fusion and the crystal lattice, we should look for a relation between the data of the 2nd and 4th columns of the table. In this case we must first of all show that the average values in the 4th column are not distributed uniformly in the interval from the smallest to the greatest average, *i. e.* from ·48 to 4·23, but that they cluster about certain values. This is

---

[7] *Phys. Ber.* ii. p. 1048 (1921).

L. Hackspill, Thèse, p. 80 (Paris, 1912).

[9] Deduced by myself from curves obtained by Charles C. Bidwell, Phys. Rev. (2) xxiii. p. 357 (1924).—For computing purposes the linear part of the curve for relative resistance, the part corresponding to the "α form," was prolonged to intersection with the melting-point ordinate; the point of intersection was assumed as the relative resistance of the "α form" at melting-point; for this point was calculated the ratio of the relative resistance of the liquid phase to the relative resistance of the "α form," and the values obtained were used in compiling the table. For my purpose only figures 3, 6, 7, and 8, those for cæsium, potassium, sodium, and lithium, could be used; whilst figures 4 and 5, both for rubidium, were unsuitable (*l. c.* p. 366).

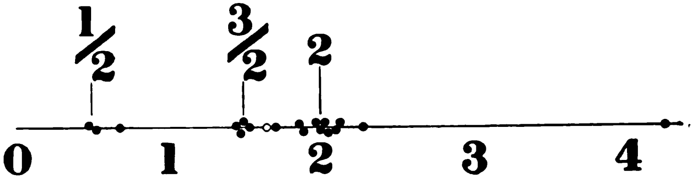
[10] Arciero Bernini, *Phys. ZS.* vi. p. 78 (1905). The value 1·91, as stated in Landolt-Börnstein, *Phys. chem. Tabellen*, p. 1052 (1923), is due to misprints in A. Bernini's Table XIII.—As the conditions of A. Bernini's experiment do not warrant the purity of the metal, his data have not been used in computing the average.

[11] This value, computed by myself from Louis Hackspill, Thèse, p. 51, fig. 4 (Paris, 1907), has not been used, in computing the average, because L. Hackspill himself retracts it in his later investigation, Thèse, p. 71 (Paris, 1912).

[12] Compare the remark to footnote 10.

[13] Compare the remark to footnote 11.

done best by constructing a distribution graph for these data as has been done on the figure, where all averages have been marked by black dots except that for aluminium, which is represented by a circle for the reason stated in paragraph 8.



5. The figure indeed displays a tendency for the average values alluded to to cluster round certain values which will be referred to as group-values. As such, disregarding the isolated value of mercury, the values 1/2, 3/2, and 2 may be taken.

6. Now, if our assumption holds good, there ought to be a relation between the group-values and the types of crystal lattices; in other words, metallic elements exhibiting common group-values should have lattices of the same type. On examining the data of the table for that purpose we find:—

7. The group-value 1/2 is common to 3 elements: bismuth, gallium, and antimony. The lattices of bismuth and antimony are of the same type, whereas that of gallium has not yet been determined. Therefore: out of 3 cases, two are in favour of the assumption made, whereas regarding one it remains questionable.

8. The group-value 3/2 is common to 6 elements: lithium, sodium, potassium, rubidium, cæsium, and aluminium. Of these, sodium and potassium have body-centred cubic lattices, lithium has probably the same lattice* while the lattices of rubidium and cæsium have not yet been determined. But considering that the elements of the second sub-group of the first groups, viz., copper, silver, and gold, have a lattice of the same type, it seems reasonable to suppose the same for the sub-group of the alkalies, *i. e.*, to assume a body-centred lattice for rubidium and cæsium. As further evidence in favour of this assumption may be mentioned the relationship between atomic numbers and properties of ions †. If, however, we turn to the lattice of aluminium, we find it to be at variance with the former:

---

* A. W. Hull, Phys. Rev. (2) x. p. 691 (1917).

† Arthur F. Scott, Journ. Ph. Chemistry, xxix. p. 306 (1925).

it is of the face-centred cubic type. Therefore: out of 6 elements, three are in favour of the assumption made, whereas regarding two it remains questionable, and one, namely aluminium, is not in accordance with it: for this reason the position of aluminium in the figure has been indicated by a mark different from those for other elements.

9. The group-value 2 is common to 9 elements: copper, silver, gold, lead, cadmium, zinc, thallium, tin, and tellurium. Of these, copper, silver, gold, and lead have face-centred cubic lattices, whilst cadmium and zinc have hexagonal lattices. But as the face-centred cubic and the hexagonal lattices referred to belong to the close-packed structure, the elements copper, silver, gold, cadmium, lead, and zinc may be united in one class—the class of the close-packed lattice. The lattice of the rhombic modification of tin, the modification which precedes the liquid phase, is still undetermined; so is the lattice of tellurium in the temperature interval immediately preceding fusion, and there is evidence for assigning to this lattice a form different from the lattice at indoor temperature *. Therefore: of 9 elements, six are in favour of the assumption made, whereas regarding three it remains questionable.

10. The group-value 4 (?) is shown only by mercury. As its lattice differs from the lattices of all other elements alluded to, this may be taken as an indirect evidence in favour of the assumption made.

11. Summarizing: Out of 19 elements, 12 elements are in favour of the statement that the rates of change of electric resistance at fusion are related to the crystal lattices of metallic elements, whereas regarding 6 elements the relation is still questionable, and divergence is exhibited by one element. The relation itself may be formulated into the following rough and ready rules:—

(1) Metallic elements, the resistances of which at fusion change in the proportion of 1 : 2, have rhombohedral hexagonal lattices of the antimony type.

(2) Metallic elements, the resistances of which at fusion change in the proportion of 3 : 2, have cubic body-centred lattices.

(3) Metallic elements, the resistances of which at fusion change in the proportion of 2 : 1, have lattices of the close-packed type.

---

* A. Guntz & W. Broniewski, *J. d. Chem. Phys.* vii. p. 485 (1909).

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

B

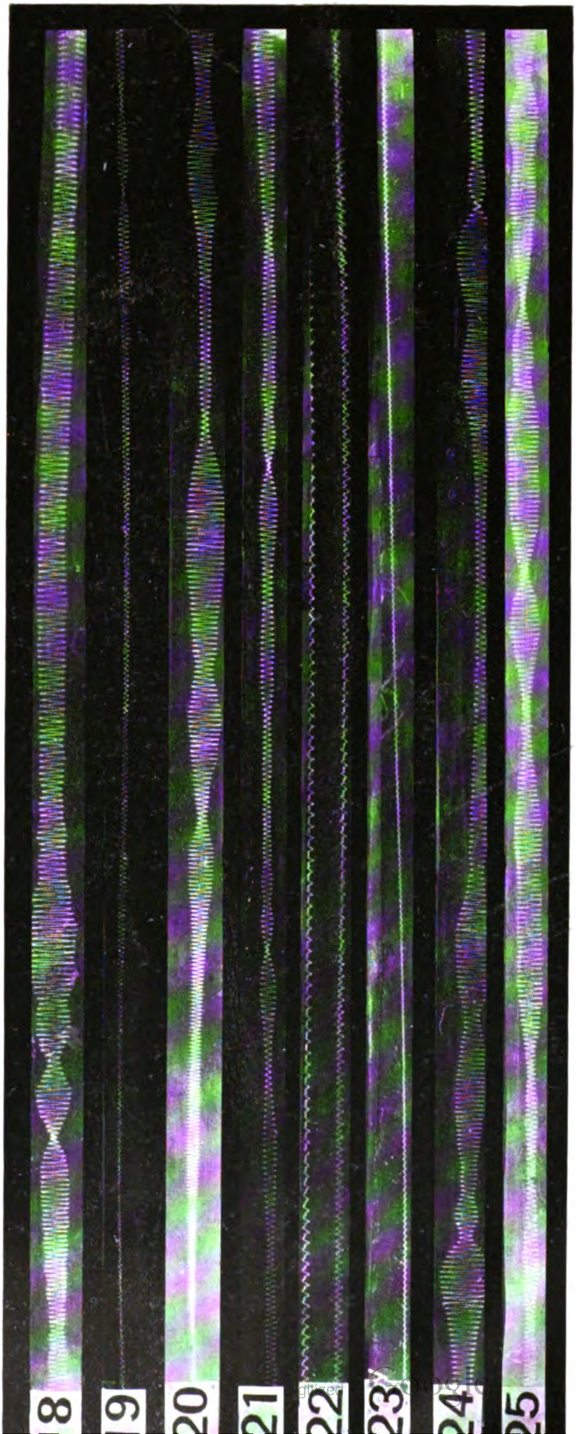


FIG. 2.

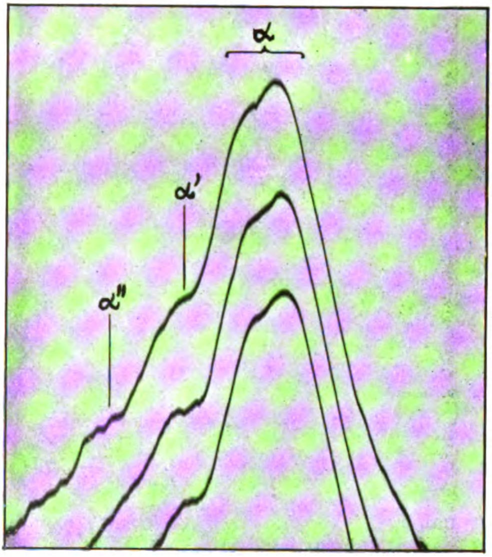


FIG. 5.

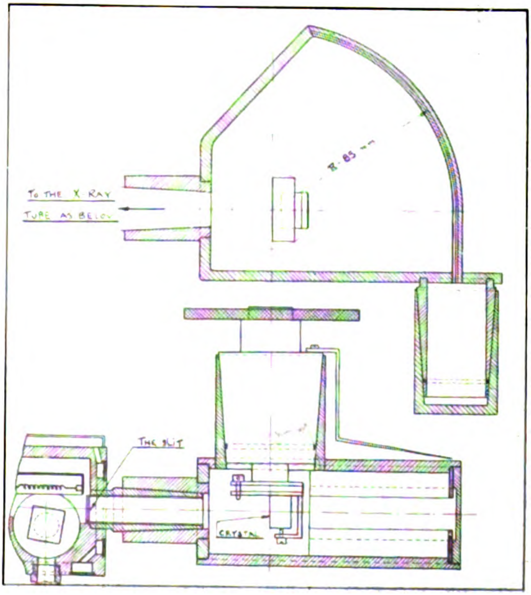
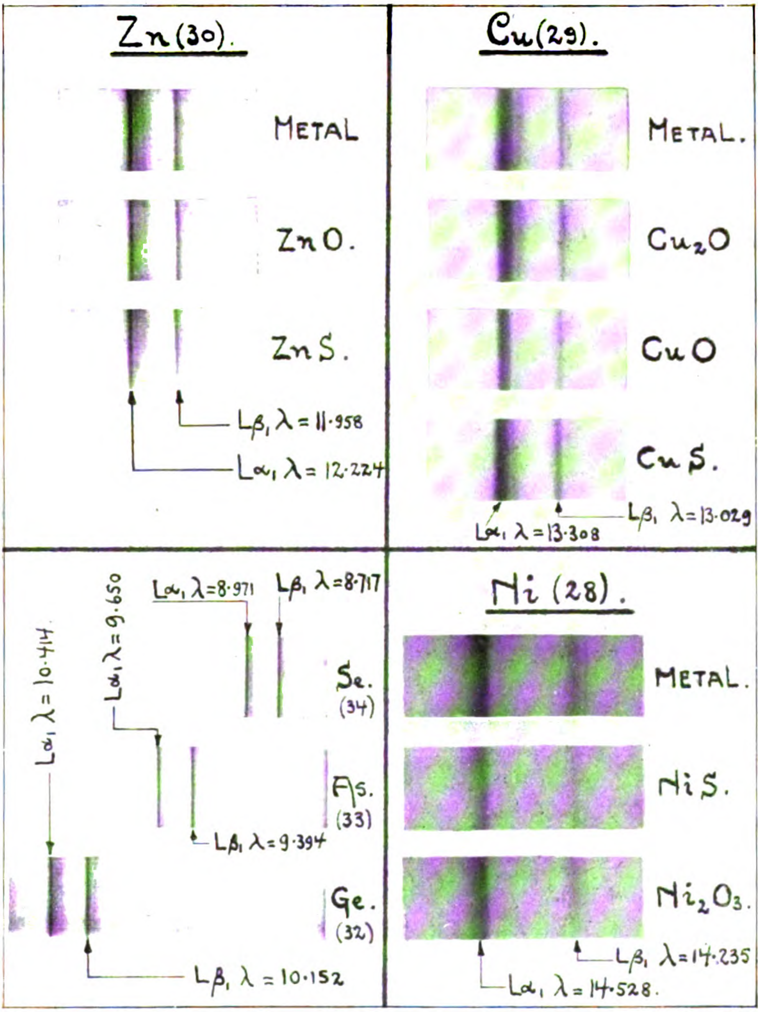
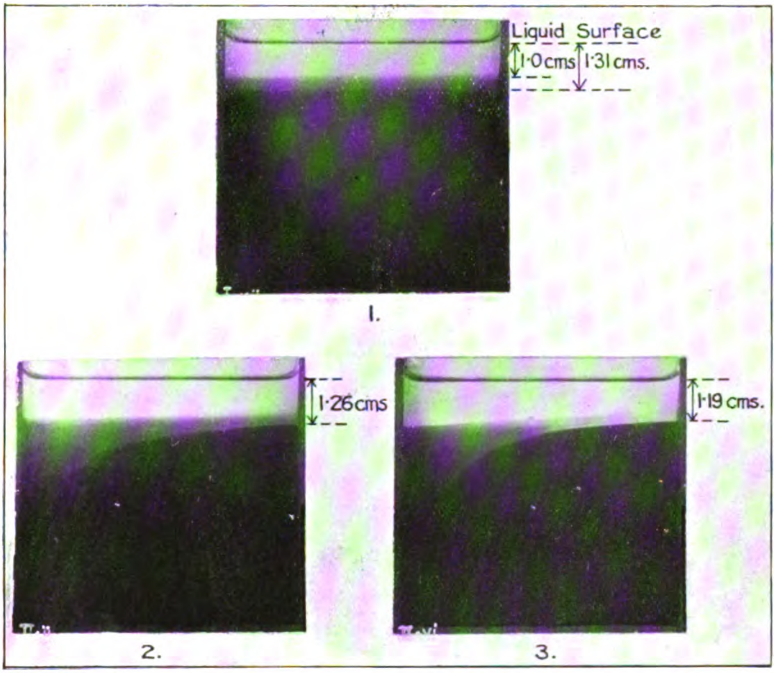


FIG. 3.

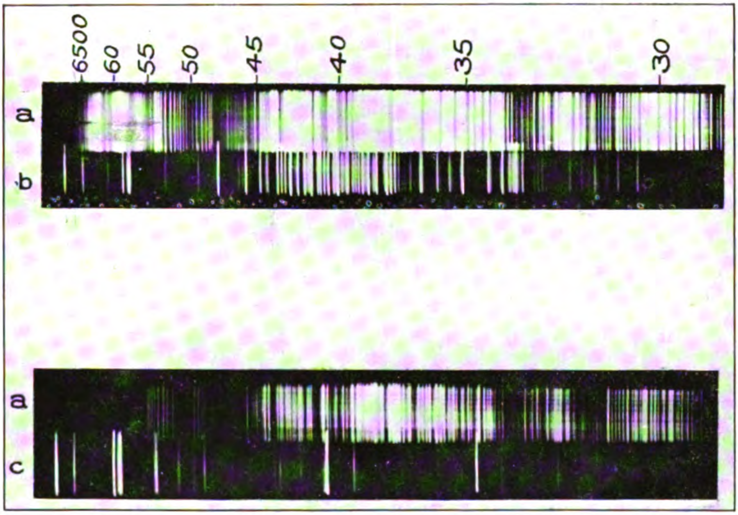


All the photograms are taken with a Gypsum Crystal.



COLLOIDAL SOLUTIONS OF COPPER.

1. After settling in dark for 18 hours (fig. 2, i.).
2. Light on right-hand side for 1 hour (fig. 2, iii.).
3. Light on right-hand side for $3\frac{1}{2}$ hours (fig. 2, vi.).



a. IRON COMPARISON SPECTRUM.
b. ENHANCED LINES OF POTASSIUM.
c. POTASSIUM ARC SPECTRUM.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

DECEMBER 1926.

CIX. *X-ray Examination of the Crystal Structure of Certain Compounds.* *By* A. Nath Sarkar, *Ph.D.* *

[Plates XXI. & XXII.]

(A) Catechol.

$C_6H_4(CH)_2$.

WHEN two hydrogens of benzene are replaced by two hydroxyl-groups, three isomeric compounds, catechol, resorcinol, and quinol, are formed.

The first compound of this group, catechol, was taken for examination by the "powder" method. Crystals of catechol grown from an aqueous solution were in the form of thin plates. The forms developed were *a* (100), *m* (110), *c* (001), and probably *x* (121); the faces of large area were *a* (100) faces.

Groth describes the crystal as follows:—

> "Monoclinic prismatic.
> $a:b:c = 1{\cdot}6086:1:1{\cdot}0229$; $\beta = 95°15'$:
> $\triangle = 1{\cdot}367$–$1{\cdot}375$."

(*Chemische Krystallographie*, vol. iv. p. 84.)

Since this crystal belongs to the prismatic class, the possible number of molecules per cell is either 1, 2, 4, 8, or 16.

The spacings of the 3 axial planes corresponding to these five possible values of H, calculated from the crystallographic data and density 1·37 (mean value), are shown below :—

---

* Communicated by Prof. Alfred W. Porter, D.Sc., F.R.S.

TABLE I.

N.	*a*-spac.	*b*-spac.	*c*-spac.
1	6·93 Å.	4·34 Å.	4·45 Å.
2	8·74 „	5·47 „	5·60 „
4	11·01 „	6·90 „	7·07 „
8	13·86 „	8·68 „	8·90 „
16	17·48 „	10·84 „	11·20 „

One of the "powder" photographs of this crystal obtained by using the K-characteristic rays of copper is shown (Pl. XXI.). The distance of the plate from the crystal powder was 3·48 cm. The spacings of the 17 diffraction lines occurring on the plate were calculated in the usual manner, and are given in the third column of the following table :—

TABLE II.

No. of line.	INT.	Obs. spac.	Calc. spac. N = 2.	Indices of Planes.	Remarks.
1.........	VS	8·73	8·74	100	
2.........	S	5·42	5·47	010	
3.........	VS	4·73	4·62	110	
4.........	W	4·38	—	—	2nd-order 100; sp. = 8·74.
5.........	MS	3·82	3·89	011	
6.........	M	3·69	3·65	$11\bar{1}$	
7.........	VVS	3·42	3·42	210	
8.........	MS	2·98	3·00	$21\bar{1}$	
9.........	WM	2·90	—	—	or 3rd-order 100; sp. = 8·74.
10.........	W	2·71	2·73	102	or 2nd-order 010; sp. = 5·47.
11.........	MS	2·64	2·60	120	or 102; sp. = 2·58.
12.........	WM	2·44	2·47	012	or 021: sp. = 2·45.
13.........	M	2·31	2·33	121 or 112	or 2nd-order 110 (this line is wide and looks double).
14.........	WM	2·07	2·08	$30\bar{2}$	
15.........	VVW	2·02	2·03	410	
16.........	VW	1·85	—	—	2nd-order $11\bar{1}$ (7); sp. = 3·65.
17.........	M	1·81	—	—	2nd-order $20\bar{1}$ (rather wide); sp. = 3·59.

The above table shows that the spacings of the planes corresponding to the first two lines on the plate agree with the full calculated spacings of the planes a (100) and b (010) corresponding to 2 molecules per cell.

As this suggested the probability of the number of molecules per cell being 2, the spacings of all simple planes were calculated on this assumption from the crystallographic data and mean density of the crystal as given by Groth. The comparison of the observed and calculated spacings shows that the presence of all the 17 lines could be accounted for.

Basic Lattice.—Table II. shows that the only axial plane which has its spacing abnormally reduced is c(001). This clearly shows that the basic lattice of the crystal cannot be $\Gamma m'$, for the abnormal spacings that arise out of each of the three cases of $\Gamma m'$ are the halvings of the spacings of all planes (hkl) when either $(h+k)$, $(k+l)$, or $(h+k+l)$ is odd ; so that each of them involves the halving of the spacings of at least two of the three axial-plane's spacings.

Space-Group.—The table further shows that planes (001), (101), $(10\bar{1})$, (201), $(20\bar{1})$, etc., *i. e.* planes ***(hol)*** when l is odd, do not produce lines at their full calculated spacings. Spacings of these planes can be halved (no other fraction being possible since the basic lattice of the crystal is Γm) only if the symmetry-plane is a glide-plane and its translation parallel to its own plane is $\frac{c}{2}$. Since the basic lattice is Γm, the symmetry-plane is a glide-plane, the number of molecules per cell is 2, and the spacing b (010) is not halved, the axis of the symmetry cannot be a screw-axis. The space-group therefore is C_{2h}^4.

From the above it follows that the molecules should possess an element of symmetry which in the present case can be either a centre of symmetry or an axis of binary symmetry.

The data given by the "powder" photograph of the crystal are not sufficient for fixing the relative positions of the two types of molecules in the unit cell, or for the differentiation between the two alternative types of possible molecular symmetry.

Since the translation of the glide-plane parallel to itself is $\frac{c}{2}$ and the number of molecules per cell is 2, the molecules are most densely packed in the a (100) plane. This accounts for the presence of the diffraction lines corresponding to the 1st-, 2nd- and 3rd-order reflexions from this plane being present on the plate, and also the cleavage plane of this crystal being parallel to *a* (100) on the assumption that cleavage follows the direction of a plane of high molecular density.

(B) POTASSIUM FERRICYANIDE.

$K_3Fe(CN)_6$.

Crystals of potassium ferricyanide belong to the monoclinic prismatic class. The forms commonly developed are *a* (100), *x* (322), *w* $(1\bar{1}1)$, *q* (011), V $(12\bar{2})$, *o* (111), and *m* (110). The plane of cleavage is parallel to *a* (100).

The crystallographic data given by Groth are as follows:—

$$\text{“}a:b:c = 1{\cdot}287 : 1 : {\cdot}8013 ; \qquad \beta = 90^\circ\ 6' ;$$

$$\Delta = 1{\cdot}849\text{–}1{\cdot}861.\text{”}$$

(Groth, *Chem. Krys.* vol. i. p. 420.)

A thin plate of the crystal with large *a* (100) faces was selected for X-ray examination by the Laue method. The crystal was so mounted that the incident beam was normal to the (100) face and the *b*-crystallographic axis vertical. The distance of the plate from the crystal was 4 cm.

The source of X-rays was a Coolidge tube with a tungsten anticathode, and the tube was run at a voltage of 60 K.V. The photograph obtained is shown in (Pl. XXI.). The number of spots occurring on the plate is comparatively few, though the length of exposure was over 30 hours. This is probably due to the fact that this compound contains both iron and potassium, so that a wide band of the spectral range which was being used was very highly absorbed in the crystal. The symmetry of the pattern is two-fold about the horizontal line of the photograph (parallel to the *c*-axis of the crystal), and characteristic of the Laue diagrams of crystals belonging to the cyclic group when the X-rays are incident normally on a crystal face containing the symmetry-axis.

The spots which lie on the horizontal line are due to planes of the type (hol) and $(ho\bar{l})$. The glancing angles for the planes reflecting these spots were obtained from their distance from the centre of the photograph, and the probable indices of the reflecting planes fixed by comparison of the observed values of the glancing angles with those calculated for th above types of planes from the crystallographic data given by Groth *.

The identification of the spots is shown in the following table ; the indices of the planes (referred to Groth's ratio) are given in the 4th and 9th columns.

TABLE III.

Spots on + side of c-axis.					Spots on − side of c-axis.				
INT.	Obs. θ.	Calc. θ.	Indices of Planes.	Correct Indices.	INT.	Obs. θ.	Calc. θ.	Indices of Plane.	Correct Indices.
VS ...	6° 25′	6° 20′	106	103	VS ...	5° 31′	5° 49′	$10\bar{6}$	$10\bar{1}$
Abs ...	—	8° 59′	104	102	Abs ...	—	8° 44′	$10\bar{4}$	$10\bar{2}$
W ...	11° 9′	10° 58′	3.0.10	305	W ...	9° 54′	10° 11′	$3.0.\bar{10}$	$30\bar{5}$
VS ...	17° 50′	17° 21′	102	101	VS ...	16° 58′	17° 9′	$10\bar{2}$	$1\bar{0}1$
Abs ...	—	24° 52′	304	302	Abs ...	—	24° 20′	$30\bar{4}$	$30\bar{2}$

In the foregoing table we observe that the plane (102) produces a very strong spot, but no spot occurs corresponding to the plane (304). This seems unaccountable (unless the reflexion from 304 is naturally very weak), for any geometrical arrangements of molecules which will abnormally reduce the spacing of (304) will also affect (102) in a similar manner. We also find that not only are the spots corresponding to the planes (103) and (105) absent, but that no spot is reflected at the proper angle for (104). The two alternative solutions suggested by the absence of reflexions from (103) and (105) cannot account for the absence of spots corresponding to the planes (104) and (304) as well. Furthermore, the total absence of a spot due to (104) cannot be attributed to the plane reflecting rays which are too weak to produce an appreciable effect on the plate, for the spacing and glancing angles for this plane are intermediate between those of (102) and (106), both of which produce strong Laue spots. It is also equally impossible to account for the total absence of reflexion from (104) on the supposition that the wave-lengths which could have contributed

---

* For $\theta_{h0l} = \cot^{-1}\left\{1{\cdot}608\frac{1}{h} + {\cdot}0016\right\} + 6'$,

$$\theta_{h0\bar{l}} = \cot^{-1}\left\{1{\cdot}608\frac{1}{h} - {\cdot}0016\right\} - 6'.$$

mostly to the intensity of the spot fall within the band of the incident beam which is highly absorbed in the crystal, because this band lies in the region of comparatively long wave-lengths.

These anomalous results can be consistently reconciled if we assume that the ratio of $b:c$ as given by Groth should be doubled (*i.e.* the true ratios are $a:b:c = 1{\cdot}287:1:{\cdot}4013$). The various reflecting planes are re-indexed according to the corrected axial ratios in the 5th and 10th columns of Table III. According to the corrected axial ratios we find that the spots corresponding to the planes (102) and (302) are absent, whereas planes (103), (101), and (305) produce Laue spots. These abnormal reflexions are no longer anomalous, for they can arise out of either of the following cases :—

(1) The plane of symmetry is a glide-plane, and the translation of the glide-plane parallel to itself is $\left(\frac{a}{2}+\frac{c}{2}\right)$. This will halve the spacings of all planes (hol) when $(h+l)$ is odd.

(2) The basic lattice is the body-centred second lattice $\Gamma m'$, when the spacings of all planes (hkl), for which $(h+k+l)$ is odd, are halved.

The indices of the planes which reflect the Laue spots lying on the vertical line through the centre of the photograph are of the type (hko). The spacings of all such planes are unaffected by case (1), but case (2) will affect some of them. The two alternative cases may therefore be differentiated from the study of indices of this type of planes and the intensity of the spots reflected by them.

Table IV. shows the identification of the 5 spots which lie on the positive side of the vertical line throughout the centre.

TABLE IV.

INT.	Obs. θ.	Calc. θ.	Indices of Plane.
W	8° 53′	8° 50′	150
M	10° 49′	11° 0′	140
VS	14° 25′	14° 23′	130
M	17° 15′	17° 15′	250
M	21° 7′	21° 14′	120

We thus find that the reflexions from all simple planes 150.....120, whether $(h+k+l)$ is odd or even, are present. This suggests the probability of the basic lattice not being $\Gamma m'$; but, as the intensity of the spots due to the planes (140), (250), and (120) is weaker than that due to (130), it is just possible that odd-order reflexions from the three former planes are really absent and the corresponding spots are due to even-order reflexions.

To settle this point definitely a gnomonic projection was made from the Laue diagram. The indices of the reflecting planes calculated from the projection did not show any indication of the halving of the spacings of planes (hkl) when $(h+k+l)$ is odd, either by the absence or by the comparative weakness of the spots reflected from such planes generally.

It was therefore concluded that the basic lattice of the crystal is Γm. (Results given later in Table V. also confirm this conclusion.)

The method adopted in this case for the determination of the number of molecules per cell requires a general idea of the relative energy in different parts of the incident radiation, and their photographic effect. They are briefly described below.

Dauvillier [*] observed that when the source of X-rays is a glass bulb, wave-lengths longer than 1·5 Å. are entirely absorbed by the thick glass walls. The general radiation curve for 60 K.V. obtained by Hull and Rice [†] using a Coolidge bulb with a tungsten target shows that the relative energy of the rays longer than ·9 Å. is very small. In the present case we can assume the contribution of wave-lengths longer than ·9 Å. to the intensity of a spot to be negligible, for they are very strongly absorbed by the crystal.

The intensity of reflexion from a certain plane as measured from the density (blackening) of the Laue spots cannot always be taken proportional to the energy of the reflected rays. Wyckoff [‡] has carefully calculated the effect of the general radiation from a Coolidge tube with a tungsten target for different maximum voltages. His curve for 60 K.V. shows that the blackening effect of wave-lengths longer than ·5 Å. is approximately proportional to their relative energy. At this point the effect begins to increase, suddenly reaching a maximum at $\lambda = {\cdot}485$ Å. (critical absorption for silver); the maximum effect is maintained roughly to $\lambda = {\cdot}4$ Å.

---

[*] Ledoux-Lebard and Dauvillier, 'La Physique des Rayons-X.'

[†] Hull and Rice, Proc. Acad. Nat. Sci. ii. (1916).

[‡] Wyckoff, Amer. Journ. Sci. l. p. 336 (1920).

After this point the blackening effect falls very rapidly (the effect of critical absorption by bromine of $\lambda = ·917$ Å. need not be considered, as energy of this wave-length is very small).

This abnormal effect on the photographic plate of certain wave-lengths affords a very convenient means of detecting the wave-lengths reflected by certain planes, for we can generally assume that the intensity of most of the strong spots produced by planes having comparatively complex indices is largely due to wave-lengths which lie between ·49 Å. and ·4 Å. for 60 K.V.

We have already found that the symmetry plane of the crystal is a glide-plane, and its basic lattice is Γm; the number of molecules per cell is therefore either 2 or 4.

Pl. XXI. shows that the spots corresponding to the rather complex planes (131), (141), and (161) are very strong, and that the spot reflected by the plane (151) is weak. The spacings of these planes corresponding to 2 and 4 molecules per cell were calculated from the corrected crystallographic data and the glancing for these planes observed. The wave-lengths reflected by each of them calculated therefrom are shown below.

TABLE V.

	131.	141.	161.	151.
N = 4	$\lambda_1 = 1·31$	$\lambda_1 = ·90$	$\lambda_1 - ·49$	$\lambda_1 = ·67$
	$\lambda_2 = ·66$	$\lambda_2 = ·45$	$\lambda_2 = ·25$	$\lambda_2 = ·34$
	$\lambda_3 = ·44$	$\lambda_3 = ·30$		
	$\lambda_4 = ·34$			
N = 2	$\lambda_1 = 1·05$	$\lambda_1 = ·71$	$\lambda_1 = ·39$	$\lambda_1 = ·53$
	$\lambda_2 = ·53$	$\lambda_2 = ·36$		$\lambda_2 = ·27$
	$\lambda_3 = ·35$			

From the foregoing discussion on the intensity of Laue spots it follows that the intensity of the spots produced by all the three planes (131), (141), and (161) could not have been very strong unless each reflected a wave-length which is photographically very effective. The above table clearly shows that this is true when N is 4, for the 3rd-, 2nd-, and 1st-order reflexions from the planes (131), (141), and (161) respectively are produced by wave-lengths all of which lie within the most effective range (·49–·4) Å. On this assumption a weak spot from the plane (151) is also accounted for. On the other hand, if N had been 2, none of these spots should have been strong (possibly excepting that due to (161)) A strong spot due to (131) also proves that the basic lattice of the crystal cannot be $\Gamma m'$.

The reflexion from the plane *b* (010) does not occur on the plate ; therefore the exact nature of the symmetry-axis could not be decided from the Laue photograph of the *a* (100) face of the crystal.

The final conclusions from the observed data are therefore that the space-group is C_{2h}^4 or C_{2h}^5, according as the axis of symmetry is a simple or screw-axis, and that the molecules are asymmetric.

(C) ALUMINIUM ACETYLACETONE.

$(C_5H_7O_2)_3Al$.

Lang * describes this crystal as follows :—

Class : Monoclinic prismatic.

Forms : *a* (100), *m* (110), *c* (001), *g'* ($\bar{1}$01), *b'* ($\bar{1}$03).

$a : b : c = 1·901 : 1 : 1·361 ; \quad \beta = 98° 54'.$

Facets belonging to the forms *g'* ($\bar{1}$01) and *b'* ($\bar{1}$03) gave very poor reflexions, and he was not satisfied that they corresponded to real faces.

Subsequent examination of the crystals by T. V. Barker † showed that the form *g'* was actually developed and that $a : g' = 66° 26'$ (not 62° 24' as observed by Lang). The crystal elements according to the new observations are therefore :—

$$a : b : c = 1·901 : 1 : 1·111.$$

A Laue photograph was taken with the rays incident normally on *c* (001) face and the *b*-crystallographic axis vertical. The pattern obtained is shown in Pl. XXII. The maximum voltage through the tube was 60–70 K.V. and the distance of the plate from the crystal 4 cm.

---

* *v.* V. Lang, *Sitzungber. d. Akad. d. Wiss.* (Wien), cxi. (2 *a*), p. 1166 (1902).

† Morgan and Drew, Trans. Chem. Soc. cxix. (ii.), p. 1064 (1921).

The identification of one of the six pairs of spots on the vertical line through the centre of the pattern is shown in the following table. The fourth column gives the indices of the corresponding planes according to the axial ratios observed by Barker.

Table VI.

INT.	Obs. θ.	Calc. θ.	Indices of Planes.	Corrected Indices.
S	6° 20′	6° 30′	081	041
M	8° 21′	8° 38′	061	031
VS	12° 15′	12° 40′	041	021
WM...........	16° 30′	16° 50′	031	032
M..............	18° 26′	18° 50′	083	043
M..............	24° 11′	24° 30′	021	011

The table shows that spots due to the planes 071 and 051 do not occur. Since strong reflexions from more complex planes (081 and 061) are present, it is improbable that the total absence of the spots from 071 and 051 is due to these planes reflecting weakly. Furthermore, in a normal case this cannot be accounted for on the supposition that the rays reflected by them are all outside the range of wave-lengths which was used, or that they had very little photographic value, for the spacing and glancing angles for 071 are intermediate between those of 081 and 061, and therefore the wave-lengths reflected by it should have an intermediate value. The same reasoning holds good for 051. However, the spots due to these planes could be absent if the basic lattice of the crystal is the *c*-face-centred lattice $\Gamma m'$, which will halve the spacings of all planes (hkl) if $(h+k)$ is odd. (Presence of a spot due to 031 might be assumed to be due to even-order reflexions from this plane.)

For further information on this point and the determination of the nature of the symmetry plane, the indices of planes reflecting the various spots on the horizontal line through the centre of the photograph were obtained in the usual manner. The identification of the spots is shown in the following table :—

TABLE VII.

Spots on − *ve* side of *a*-axis.					Spots on + *ve* side of *a*-axis.				
INT.	Obs. θ.	Calc. θ.	Indices of Planes.	Correct Indices.	INT.	Obs. θ.	Calc. θ.	Indices of Planes.	**Correct Indices.**
Abs. ...	—	3° 25′	$80\bar{1}$	$40\bar{1}$	VS ...	8° 21′	8° 54′	100	**10**
VW ...	7° 10′	7° 31′	$60\bar{1}$	$30\bar{1}$	VW ...	16° 37′	17° 38′	11.0.1	**11. 0.2**
Abs ...	—	8° 58′	$11.0.\bar{2}$	$11.0.\bar{4}$	W......	18° 12′	19° 15′	9.0.1	**902**
M......	10° 25′	10° 48′	$50\bar{1}$	$50\bar{2}$	VW ...	21° 0′	22° 0′	701	**702**
S	12° 18′	12° 46′	$90\bar{2}$	$90\bar{4}$					
VS ...	14° 54′	15° 28′	$40\bar{1}$	$20\bar{1}$					
WM...	18° 7′	18° 4′	$70\bar{2}$	$70\bar{4}$					
W ...	19° 20′	19° 56′	10.0.3	$50\bar{3}$					
W ...	22° 30′	22° 47′	$30\bar{1}$	$30\bar{2}$					

The absence of reflexion from the planes 10.0.1 and 801 and $80\bar{1}$, and the presence of a very weak spot corresponding to $60\bar{1}$, apparently indicate the symmetry-plane being a glide-plane and its translation parallel to its own plane either $\frac{c}{2}$ or $\left(\frac{a}{2}+\frac{c}{2}\right)$; but the deduction is improbable, for spots due to the planes $50\bar{1}$, $40\bar{1}$, $30\bar{1}$, etc., are present, and it does not account for the absence of a spot from $70\bar{1}$. Results given in the above table furthermore show that the basic lattice of the crystal cannot be the *c*-face-centred lattice $\Gamma m'$ which seemed probable from the study of Table VI.

If we assume the ratio of $b : c$ to be double of Barker's ratio, the anomalous nature of reflexion from the planes of the type (*okl*) and (*hol*) disappears. The indices of the planes given in Tables VI. and VII. have been re-indexed according to the corrected axials ($a : b : c = 1901 : 1 : 2{\cdot}222$) in separate columns of the tables headed "Correct Indices."

In Table VII. we observe that, according to the corrected axial ratios, spots corresponding to planes 501, 401, $40\bar{1}$, $30\bar{1}$, *i.e.* planes (*hol*), when l is odd (excepting $20\bar{1}$ and $50\bar{3}$), are absent, and that reflexions from more complex planes such as

$50\bar{2}$, $90\bar{4}$, $70\bar{4}$, and $30\bar{2}$, *i. e.* planes $(h0l)$, when l is not odd, occur. This indicates that the plane of symmetry is a glide-plane and its translation parallel to itself is $\frac{c}{2}$. Spots corresponding to the planes $20\bar{1}$ and $50\bar{3}$ are exceptions, but they were found to be due to even-order reflexions from these planes.

Though the results of Tables VI. and VII. suggest the improbability of the basic lattice of the crystal being $\Gamma m'$, the point could be definitely settled when the number of molecules per cell is determined and the intensities of the spots produced by certain general planes (hkl) are compared with the wave-lengths reflected by them. Accordingly, the indices of the planes reflecting the various Laue spots were calculated from a gnomonic projection made out of the Laue diagram.

It will be noticed that though the Laue diagram (Pl. XXII.) shows a two-fold symmetry about the horizontal line, the distances from the centre of the pattern of spots reflected by two corresponding planes (hkl) and $(h\bar{k}l)$ are not exactly equal. This is evidently due to the fact that the crystal face $c\,(001)$ was not quite normal to the incident beam, but rotated through a small angle about the a-axis of the crystal. For example, the distances of the spots reflected by the planes $4\bar{1}\bar{2}$ and $41\bar{2}$ from the centre are respectively 2·10 cm. and 2·04 cm.; and we find that the spot corresponding to $4\bar{1}\bar{2}$ is weak, whereas that due to $41\bar{2}$ is very strong. The spacing and grating elements of these planes are the same; and since only the glancing angles for them are different, it is evident that one of the wave-lengths reflected by $4\bar{1}\bar{2}$ should be just outside the critical point at which the blackening effect of the rays begins to fall abruptly, *i. e.* it should be just longer than ·485 Å. (the critical absorption of silver), and that the corresponding order of reflexion from $41\bar{2}$ should be within the range of wave-lengths which is photographically very effective.

The spacing of the plane $41\bar{2}$ (or $\bar{4}\bar{1}2$) calculated from the corrected axial ratios and density = 1·267 is 3·05 Å., and the glancing angles for $4\bar{1}\bar{2}$ and $41\bar{2}$ as calculated from the distances of the corresponding spots are 13° 50′ and 13° 30′ respectively. The wave-lengths producing the 1st-, 2nd-, and 3rd-order reflexions of $4\bar{1}\bar{2}$ (calculated from $n\lambda = 2d\,.\sin\theta$) are 1·46, ·73, and ·488 Å., and those of $4\bar{1}\bar{2}$ are 1·42, ·71, and

475 Å. respectively. Since the 3rd-order spectrum of $\bar{4}\bar{1}2$ is produced by $\lambda = \cdot 488$ Å., which is just beyond the critical absorption of silver, the intensity of the corresponding Laue spot is weak. A strong spot corresponding to $41\bar{2}$ is also accounted for, since the 3rd-order reflexion from this plane is due to $\lambda = \cdot 475$ Å., which is well within the range of wave-lengths producing maximum photographic effect. It is therefore concluded that the number of molecules per cell is 4.

Since the intensity of the spot due to the plane $41\bar{2}$ is mostly due to the 3rd-order reflexion, the basic lattice of the crystal cannot be $\Gamma' m$, for each of four cases of $\Gamma' m$ will halve the spacing of $41\bar{2}$, and in consequence the 3rd-order reflexion from this plane should have been absent.

The final conclusions from the results given by the Laue photograph of this crystal are therefore that the molecules are asymmetric and the space-group C_{2h}^4 or C_{2h}^5, according as the symmetry-axis is a simple or a screw-axis.

As the reflexion from the *b* (010) plane does not occur on the plate, the exact nature of the symmetry-axis could not be determined from the annexed pattern (Pl. XXII.). But Mr. Astbury has kindly supplied me with some data obtained with an ionization spectrometer. He obtains the value 3·705 Å. for the spacing of the *b* (010) plane. The full calculated spacing of this plane corresponding to N = 4 is 7·425 Å. Thus the *b*-spacing is halved, and therefore the axis is a screw-axis and the space-group C_{2h}^5.

In conclusion, I wish to thank Prof. A. W. Porter, F.R.S., for his direction and advice, and to express my indebtedness to Mr. J. H. Smith, M.Sc., for his many helpful suggestions.

CX. *The Making of a Salt Haze.*

By J. S. Owens, *M.D., A.M.I.C.E.*[*]

I OBSERVED recently an interesting phenomenon which, I think, might be termed the birth of a salt haze. On March 19th, 1926, on board the Booth liner 'Hildebrand,' we were off the coast of Spain, south of Cape Finisterre; it was a bright sunny morning, with a light wind from the south-east, that is off the land. A long swell was breaking on the rocky coast and throwing up a great deal of spray where partly submerged rocks occurred. The coast itself was partly obscured by a white haze nearly up to the tops of the hills, which appeared about 400 or 500 feet high, but this was definitely denser near the sea-level. The visibility out to sea was very good. It was 9 A.M. and the sun was over the land, the sky clear of cloud except over the land. At certain places along the coast, over projecting rocks where the spray formation was very marked, the haze referred to was definitely denser than at other points; all such parts were overhung by fairly well-defined patches of haze.

---

[*] Communicated by the Author.

While passing through the haze on the 19th I took some records with the jet dust counter [*], and a 1000 c.c. record was distinctly visible with the naked eye. Examination under the microscope showed that the record consisted practically entirely of soluble crystalline matter. When first examined the line of the record was covered with small drops, which, on warming, dried and left well-defined crystals, chiefly skeletal and fern-like, some very small and indefinite in shape. There was a star-shaped crystal of eight rays, outside diameter about 4 microns; one imperfect star with one long ray, like a dagger blade, about the same size, but the crystals were mostly skeletal.

On the following morning, farther south along the same coast, it is perhaps of significance to note that there was a dense fog which gradually cleared as the sun got up, so that it was practically gone at 9 A.M. At this time I took a wet and dry bulb observation which showed a dry bulb temperature of 54·5° F. and wet 50° F. This represents a relative humidity of 71 per cent., which is therefore a little below the humidity at which sodium chloride deliquesces [†], and it seems to convey the suggestion that the presence of salt crystals in the air may have been responsible for the fog.

On several occasions, haze composed practically entirely of salt crystals has been found in the vicinity of the sea. Such hazes have already been described in the Proceedings of the Royal Society, A, cx. (1926), and in the Ninth and Tenth Annual Reports of the Advisory Committee on Atmospheric Pollution.

It seemed worth while finding, if possible, the humidity conditions under which the actual crystals obtained in the record taken on the 19th would deliquesce. The cover glass with its record was therefore removed from its mounting ring and set up on three wax pellets above a glass slip, leaving about 2 mm. air-space between the record and the slip, the record being on the face of the cover glass next the slip. The crystals were observed under the microscope during different conditions of humidity as it altered naturally. The humidity was measured by an Assmann psychrometer, the bulbs of which were placed in close proximity to the record.

---

[*] Proc. Roy. Soc. A, ci. (1922).

[†] "Condensation of Water from the Air upon Hygroscopic Crystals," by J. S. Owens, Proc. Roy. Soc. A, cx. (1926).

The first observation showed the record to consist of drops only, the humidity was then 77 per cent. It fell to 74 per cent. without any change in the drops. The next observation was at a humidity of 51 per cent., and all the drops had disappeared, leaving dry crystals; this condition persisted when the humidity rose again, and the last observation was at 64 per cent., the crystals being all dry. During the last observation, on breathing near the record the trace became immediately converted into a line of drops, which disappeared again in three or four seconds, showing the rapid response to the surrounding conditions.

The crystalline matter present in the air on the 19th was capable of collecting moisture, or retaining it, at 74 per cent. relative humidity at a temperature of 61·5° F., but lost its moisture at 64 per cent. at a temperature of 58° F. This is significantly similar to the behaviour of crystals of sea salt when observed under changing conditions of humidity.

The above observations may throw some light upon the reputation which the Spanish and Portuguese western coasts have for fogs. It is evident that if the atmosphere contains large numbers of crystals which deliquesce at humidities 25 per cent. below saturation, the conditions for fog formation must be exceptionally favourable. The nature of the coast and the exposure to the Atlantic swell is such that it must be a prolific factory for salt haze, and apparently this may easily become converted into a thick fog.

The method of formation of such a haze is worth considering. It appears probable that the origin of the haze may have some effect upon the distribution of the different salts forming it. It is well known that sea salt is a mixture consisting mainly of sodium chloride but with considerable proportions of other salts, such as magnesium chloride. If a salt haze is developed from spray thrown up from the surface of the sea under the action of the wind, the crystals resulting from the evaporation of the liquid suspended in the air will be composed of a mixture of all salts present. If we picture a drop of solution of a mixture of sodium and magnesium chlorides drying while suspended in the air, the less hygroscopic sodium chloride will doubtless crystallize out and form a solid core to the drop when the humidity falls below about 75 per cent.; but at this stage there would be surrounding the core a more concentrated solution of magnesium chloride, and this would not evaporate until the air became much drier. Thus we might expect a core of sodium chloride with surface crystals of magnesium chloride. With such a formation it is not easy to see how a selective deposit could take place unless the surface crystals of the more hygroscopic salt became separated in some way from the less hygroscopic core.

There are, however, other ways in which it is probable the salt haze is generated, which might produce a suspension of crystals in which the different salts were separated. For example, in the case of flat sandy foreshores where a great expanse of sand is exposed at low water there is usually a marked drift of sand under the action of the wind. This is responsible for the formation of sand dunes which often border the coast near such foreshores. The wind is capable of picking up sand while the latter is wet with sea water, and the sand may often be observed drifting in a dense layer over the surface of the damp foreshore. The sand particles being wetted with sea water, under suitable conditions no doubt the surfaces of the grains become coated with minute crystals of sea salts; these crystals may be detached by the rubbing of the sand grains together under the action of the wind, and thus a haze of very fine crystalline matter be distributed in the air. Such a haze would probably have the crystals of the different salts to a great extent separated from each other, and as the humidity of the air alters there would probably be a selective settlement of the more hygroscopic particles before the others. If, for example, we picture conditions when the relative humidity is over 75 per cent. for some time and the air is still, it would seem to be probable that all the salts which deliquesce at humidities above this would tend to settle out by virtue of their increased mass after deliquescence, thus leaving behind the salts which remain dry under those conditions.

I do not think we can assume, as has been done (Kohler) *, that salts derived from the sea necessarily maintain the same composition when suspended in the air.

---

* Hilding Kohler, "The Condensation of Vapour in the Atmosphere," Geophysical Publications, vol. ii., Danish Geophysical Commission, 1921.

Haze at Holme, Norfolk.

The following observation was made on August 31st and September 1st, 1926, on the coast at Holme, which is situated on the southern coast of the Wash:—A strong wind was blowing in from the sea on Tuesday, August 31st; the direction was about NW'N., and on Wednesday this veered to nearly due North. The velocity was approximately 20 miles per hour, as measured by the flight of thistledown over a measured distance. The sea was rough and there was a large quantity of sand blowing on the foreshore. A dense haze covered the land, the limit of visibility being about 5 miles. The same was true over the sea, the horizon being very hazy. The weather was fine, except that on the night of Tuesday, August 31st, there was a slight fine rain.

On Wednesday, September 1st, a trap was set up with the object of catching some of the haze particles. This trap was made from a tin, about 100 millimetres diameter and 120 millimetres long, and open at one end. In the middle of the closed end of this tin a hole about 2 millimetres diameter was punched, and it was set up with the open mouth facing the wind with a microscope slide wedged about 2 millimetres behind the hole, so that the jet of air passing out through the hole in the bottom struck the microscope slide. The apparatus was set up about 100 yards landward of the foreshore. The tides at the time were neaps, and a large area of sand on the foreshore was exposed; the sand, as stated above, was drifting with the wind.

The first slide was put in at 10.30 A.M., and at 11.15 A.M. a patch visible to the naked eye had formed opposite the hole. The slide was removed at 12.30 P.M. and, examined under a low power, showed mostly drops, which disappeared on warming the slide, leaving what was apparently crystalline deposit behind. Slide No. 2 was put in at 12.30 P.M. and removed at 3.35 P.M. The haze during the whole time remained about the same. On examining these slides under the microscope on my return to London, the visible patches were seen to consist almost entirely of drops. At the time of examination the humidity was taken with an Assmann psychrometer, the wet bulb was 63·7° F., the dry 67·4° F., indicating a relative humidity of 80 per cent. On warming the slides gently the drops disappeared and crystals were formed. These were mostly skeletal crystals with arms at 90°. The crystals were allowed again to deliquesce, when a few rhomboid crystals were found which did not liquefy. On being re-warmed, a large number of well-formed squares and rectangular plates appeared. The second slide showed the same appearance, except that there were large numbers of rhomboid crystals scattered through the drops, and, on drying, numbers of cubical crystals having sides up to 24 microns diameter became visible—evidently sodium chloride,—but there were also a number of skeletal crystals with 90° arms.

It is evident, therefore, that the haze contained, if it did not entirely consist of, large numbers of salt crystals, and as they were probably at the time partly if not completely deliquesced, it appears to be a somewhat interesting condition —probably the transition state from a haze of dry crystals to a fog of liquid drops. It is important to note that the relative humidity at which the crystals were found to have deliquesced was 80 per cent., while common salt is known to deliquesce at 74 per cent. to 75 per cent. relative humidity. The sea during the observation was rough, and doubtless one of the sources of the haze particles was the spray carried in the wind, but there was as well a large expanse of open foreshore over which sand was blowing, and this sand being wet with sea water doubtless set free salt particles into the wind. Particles so set free from blowing sand need not have the same composition as sea salt, as the selective deliquescence of the salts would come into operation, some adhering to the sand particles when wet, while others might be crystalline and free to be knocked off by the impact of the sand particles with each other.

CXI. *The General Theory of the Sensation of Flickers in Peripheral and Central Vision.* By P. LASAREFF, *Member of the Academy of Sciences (Leningrad), Director of the Institute of Physics and Biophysics (Moscow)* *.

IN my publications from the year 1914 I have demonstrated that many phenomena observed with Flickers can be explained if we apply the ionic theory of stimulation developed by myself †.

For the moment at which we obtain a continuous sensation of illumination, the number of light interruptions in a second N, the intensity of the light J, and the time t of darkness adaptation after strong illumination of the retina are connected by the following formula :

---

* Communicated by the Author.

† Article by P. Lasareff in the special publication of the Ledentzov Society in Moscow, with an English resumé, 1914; later the same theory was published in my book 'Recherches sur la théorie ionique de l'excitation' (Moscou, 1918), and in P. Lasareff, 'Ionentheorie der Reizung' (Bern und Leipzig, 1923).

$$(\mathrm{N}-\mathrm{N}_0)\sqrt{4\pi^2\mathrm{N}^2+\alpha_2^2} = \alpha_1 k \mathrm{J} \mathrm{C}_0(1-e^{-\alpha_3 t})\mathrm{A}.$$

N_0, α_2, α_3, C_0, α_1, and A are constants ; k is the constant of absorption.

The above formula may be written in another way :

$$\log(\mathrm{N}-\mathrm{N}_0)+\tfrac{1}{2}\log(4\pi^2\mathrm{N}^2+\alpha_2^2) = \log \mathrm{J}+\mathrm{B}. \quad . \quad (1)$$

B is a constant.

Later Allen proposed another empirical formula connecting N and J [*]. This formula has the form

$$\mathrm{N} = \mathrm{A}\log \mathrm{J}+\mathrm{B}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

A and B are constants which can be determined from experimental data.

In Allen's experiments, which confirmed excellently formula (2), the variations of N and J are very large, and it is necessary to investigate the connexion between the formulæ (1) and (2).

This question is the purpose of the present paper.

§ 1. *General Theory of the Photochemical Phenomena during periodical illumination of the retina.*

We will first investigate the influence of the periodical illumination of the layer of sensitive pigment. The concentration of this pigment is C and the concentration of the ionized products of photochemical reaction is C_1'.

As I have shown in my previous works [†], the velocity of the reaction which gives the stimulating ionized products must be proportional to the absorbed energy, which is, when C is small, equal to $\alpha_1 k \mathrm{JC}$ (J is the periodically varying intensity of light). At the same time as the destruction of the pigment we have, in the retina, the process of restoration of sensitive pigment. As I have demonstrated, this process has a velocity $-\alpha_2 \mathrm{C}_1'$. We have therefore for the process taking place in the retina during the action of light on the retina the following differential equation for the velocity of the reaction :

---

[*] F. Allen, Phil. Mag. ser. 6, xxxviii. p. 81 (1919).

[†] P. Lasareff, Pflüger's *Archiv*, cliv. p. 459 (1913) and clv. p. 310 (1914). P. Lasareff, 'Recherches sur la théorie ionique de l'excitation,' p. 86 (Moscou, 1918). P. Lasareff, 'Ionentheorie der Reizung,' p. 13 (Bern und Leipzig, 1923).

$$\frac{dC_1'}{dt} = \alpha_1 kJC - \alpha_2 C_1' ;$$

or putting $J = J_0(1 - \sin nt)$, where $n = 2\pi N$, we have

$$\frac{dC_1'}{dt} + \alpha_2 C_1' = \alpha_1 k J_0 C(1 - \sin nt). \quad . \quad . \quad . \quad (3)$$

The oscillation of C during continuous sensation is very small and the change in C, which produces the adaptation, is very slow, and we can therefore assume that during the experiment C is constant.

With this hypothesis we obtain the solution of (3) in the form

$$C_1' = \frac{\alpha_1}{\alpha_2} kJ_0 C - \frac{\alpha_1 k J_0 C}{\sqrt{\alpha_2^2 + n^2}} . \sin(nt - \phi), \quad . \quad . \quad . \quad (4)$$

$\tan\phi$ being equal to $\frac{n}{\alpha_2}$.

This equation gives us the law for the variation of concentration of the products during periodical illumination of the retina.

The amplitude of the variation of concentration is equal to

$$A = \frac{\alpha_1 k J_0 C}{\sqrt{\alpha_2^2 + n^2}}.$$

If we take into consideration that C varies very slowly in the darkness after the complete destruction of the pigment by the action of intensive light, we can calculate that this variation can be expressed by the formula* :

$$C = C_0(1 - \gamma e^{-\alpha_3 t}),$$

γ being a constant dependent on the intensity of the light J, which has acted on the retina (if $J = \infty$, $\gamma = 1$). We obtain therefore

$$A = \frac{\alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t})}{\sqrt{\alpha_2^2 + n^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

---

* See P. Lasareff, Pflüger's *Archiv*, clv. p. 311 (1914). P. Lasareff, 'Recherches,' p. 106.

§ 2. *The conditions which must be fulfilled in order to obtain a continuous sensation during interrupted illumination of the retina.*

If we obtain a minimum sensation from flickers, the amplitude of variation of the concentration of ions (5) must be connected in the following way with the frequency $n=2\pi\mathrm{N}$, $\mathrm{A}=\phi(n)$. We can therefore express this connexion in the form

$$\mathrm{A} = \phi(n) = \frac{\alpha_1 k \mathrm{J}_0 \mathrm{C}_0 (1-\gamma e^{-a_3 t})}{\sqrt{\alpha_2^2+n^2}}, \quad . \quad . \quad . \quad (6)$$

or

$$\phi(n)\sqrt{\alpha_2^2+n^2} = \alpha_1 k \mathrm{J}_0 \mathrm{C}_0 (1-\gamma e^{-a_3 t}). \quad . \quad . \quad . \quad (7)$$

These formulæ (6) and (7) are the most general expressions for the conditions necessary for a continuous sensation during the action of flickering light, and every empirical formula giving a good agreement with experiment can be included in these formulæ. We will consider separately the three cases studied by myself and one case studied by F. Allen.

(1) *The first formula of Lasareff.*

If we make the simplest hypothesis about the form of $\phi(n)$ and if we put $\phi(n)=\mathrm{R}n$ (R is a constant) we obtain

$$n\sqrt{\alpha_2^2+n^2} = \frac{\alpha_1 k \mathrm{J}_0 \mathrm{C}_0}{\mathrm{R}}(1-\gamma e^{-a_3 t})^{*} . \quad . \quad . \quad . \quad (8)$$

(2) *The second formula of Lasareff.*

We can give to the function $\phi(n)$ a more complicated form. For instance, we can put $\phi(n)=\mathrm{R}(n-n_1)$; n_1 is a constant. In this case

$$(n-n_1)\sqrt{\alpha_2^2+n^2} = \frac{\alpha_1 k \mathrm{J}_0 \mathrm{C}_0}{\mathrm{R}}(1-\gamma e^{-a_3 t}). \quad . \quad . \quad (8a)$$

This is the second type of equation proposed by myself.

(3) *The generalized formula of Allen.*

In order to satisfy the empirical formula of Allen we can put $\phi(n)\sqrt{\alpha_2^2+n^2}=\mathrm{R}e^{pn}$; R and p are constants.

The formula (7) gives us

$$\mathrm{R}e^{pn} = \alpha_1 k \mathrm{J}_0 \mathrm{C}_0 (1-\gamma e^{-a_3 t}).$$

---

[*] P. Lasareff, Publication of the Ledenzov Society (*loc. cit.*). P. Lasareff, 'Recherches sur la théorie ionique de l'excitation' (*loc. cit.*).

This equation can be given another form:

$$\log R + pn \log e = \log J_0 + \log(1-\gamma e^{-\alpha_3 t}) + \log \alpha_1 k C_0,$$

or

$$n = \frac{1}{p \log e} \log J_0 + \frac{1}{p \log e} \cdot \log(1-\gamma e^{-\alpha_3 t}) + \frac{1}{p \log e} \cdot \log \alpha_1 k C_0 - \frac{1}{p \log e} \cdot \log R. \quad (9)$$

If the conditions of adaptation are not variable the formula is identical with Allen's equation.

(4) *The third formula of Lasareff.*

We can assume that the amplitude $A=\phi(n)$ satisfies the following conditions.

A increases with n, and we can assume that the relative increase of A, equal to $\frac{dA}{A}$, is proportional to dn. If p is a constant, we have

$$\frac{dA}{A} = pdn \quad \text{or} \quad A = Re^{pn},$$

R being a constant.

Substituting this value of A in formula (7) we have

$$Re^{pn}\sqrt{\alpha_2^2+n^2} = \alpha_1 k J_0 C_0 (1-\gamma e^{-\alpha_3 t}) \quad . \quad . \quad . \quad (10)$$

This is the formula deduced by myself.

In conclusion we will show that the general equation

$$\phi(n) = \frac{\alpha_1 k J_0 C}{\sqrt{\alpha_2^2+n^2}} \quad . \quad . \quad . \quad . \quad . \quad (10\,a)$$

can be made to give some interesting general results, without precise determination of the form of function $\phi(n)$. Indeed, as I have proved*, during the continuous action of light having a constant intensity the concentration of stimulating ions C_1' is equal to

$$C_1' = \frac{\alpha_1}{\alpha_2} kJC.$$

At the threshold of stimulation $C_1'=B$ [B is a constant], and the sensibility $E=\frac{1}{J}$ is in this case equal to

$$E = \frac{\alpha_1 k C}{\alpha_2 B},$$

and from this we get

$$\alpha_1 k C = \alpha_2 B E.$$

---

* P. Lasareff, Pflüger's *Archiv*, liv. p. 464 (1913). P. Lasareff, 'Recherches sur la théorie ionique de l'excitation,' p. 88. P. Lasareff, 'Ionentheorie der Reizung,' p. 17.

Substituting this value in the equation (10 *a*) we have

$$\phi(n)=\frac{\mathrm{BEJ}_0}{\sqrt{1+\left(\frac{n}{\alpha_2}\right)^2}},$$

or

$$\phi(n)\sqrt{1+\left(\frac{n}{\alpha_2}\right)^2}\cdot\frac{1}{\mathrm{B}}=\mathrm{EJ}_0.$$

We conclude from this that if the product of sensibility E and the amplitude of intensity of interrupted light J_0 is constant, the frequency of interruption giving a continuous sensation remains the same.

We can formulate the results obtained above as follows:—

$$\left.\begin{array}{l}
\text{(a) The first formula of Lasareff :}\\
\qquad n\sqrt{\alpha_2^2+n^2}=\frac{1}{\mathrm{R}}\alpha_1k\mathrm{J}_0\mathrm{C}_0(1-\gamma e^{-\alpha_3t}).\\
\text{(b) The second formula of Lasareff :}\\
\qquad (n-n_1)\sqrt{\alpha_2^2+n^2}=\frac{1}{\mathrm{R}}\alpha_1k\mathrm{J}_0\mathrm{C}_0(1-\gamma e^{-\alpha_3t}).\\
\text{(c) The generalized formula of Allen :}\\
\qquad e^{pn}=\frac{1}{\mathrm{R}}\alpha_1k\mathrm{J}_0\mathrm{C}_0(1-\gamma e^{-\alpha_3t}).\\
\text{(d) The third formula of Lasareff :}\\
\qquad e^{pn}\sqrt{\alpha_2^2+n^2}=\frac{1}{\mathrm{R}}\cdot\alpha_1k\mathrm{J}_0\mathrm{C}_0(1-\gamma e^{-\alpha_3t}).
\end{array}\right\}\quad .\quad (12)$$

If n_0 is the value of n corresponding to the maximum adaptation (complete darkness adaptation), we obtain :

$$\left.\begin{array}{ll}
(\mathrm{a}_1) & n_0\sqrt{\alpha_2^2+n_0^2}=\frac{1}{\mathrm{R}}\alpha_1k\mathrm{J}_0\mathrm{C}_0.\\
(\mathrm{b}_1) & (n_0-n_1)\sqrt{\alpha_2^2+n_0^2}=\frac{1}{\mathrm{R}}\alpha_1k\mathrm{J}_0\mathrm{C}_0.\\
(\mathrm{c}_1) & e^{pn_0}=\frac{1}{\mathrm{R}}\alpha_1k\mathrm{J}_0\mathrm{C}_0.\\
(\mathrm{d}_1) & e^{pn_0}\sqrt{\alpha_2^2+n_0^2}=\frac{1}{\mathrm{R}}\alpha_1k\mathrm{J}_0\mathrm{C}_0.
\end{array}\right\}\quad .\quad .\quad (12\,a)$$

Dividing (a) by (a_1), (b) by (b_1), (c) by (c_1), and (d) by (d_1), we find :

$$\left.\begin{array}{l}
\text{(A) (First formula of Lasareff)}\\
\qquad\qquad\dfrac{n\sqrt{\alpha_2^2+n^2}}{n_0\sqrt{\alpha_2^2+n_0^2}}=1-\gamma e^{-a_3t}.\\
\text{(B) (Second formula of Lasareff)}\\
\qquad\qquad\dfrac{(n-n_1)\sqrt{\alpha_2^2+n^2}}{(n_0-n_1)\sqrt{\alpha_2+n_0^2}}=1-\gamma e^{-a_3t}.\\
\text{(C) (Generalized formula of F. Allen)}\\
\qquad\qquad\dfrac{e^{pn}}{e^{pn_0}}=1-\gamma e^{-a_3t}.\\
\text{(D) (Third formula of Lasareff)}\\
\qquad\qquad\dfrac{e^{pn}\sqrt{\alpha_2^2+n^2}}{e^{pn_0}\sqrt{\alpha_2^2+n_0^2}}=1-\gamma e^{-a_3t}.
\end{array}\right\}\quad .\;.\;(13)$$

§ 3. *The comparison of the theoretical formulæ with the experiments.*

All the above formulæ (13) give more or less complicated functions of n which must all be equal to $1-\gamma e^{-a_3t}$, expressing the curve of darkness adaptation, after the action of light. These formulæ (13) must be independent of the wave-length of the light producing the flicker. If, therefore, we find for all wave-lengths of interrupted light that the expression $1-\gamma e^{-a_3t}$ is equal to the particular function of n we are considering, we conclude that the theory coincides with experiment.

In order to test the formulæ (13) we may use the very precise data obtained by M. Schaternikoff [*]. For this case the intensity of the light producing the light adaptation was great, and therefore $\gamma=1$. The results of the experiments of Schaternikoff and the theoretical formula are given in Tables I., II., III., IV. In all cases α_2 is equal to 9·75 [†].

We see that in order to satisfy the condition (13) we must choose different values of a_3, which are for $\lambda=510{\cdot}5$

---

[*] M. Schaternikoff, *Zeitschr. f. Psychologie und Physiolog. der Sinnesorg.* xxix. p. 241 (1902).

[†] P. Lasareff, Publication of Ledentzov Society (*loc. cit.*).

TABLE I.

	$\lambda = 510{\cdot}5\ \mu\mu$.		$\lambda = 589\ \mu\mu$.		$\lambda = 670{\cdot}8\ \mu\mu$.	
	$1-e^{-a_3t}$.	$\frac{n\sqrt{a_2^2+n^2}}{n_0\sqrt{a_2^2+n_0^2}}$.	$1-e^{-a_3t}$.	$\frac{n\sqrt{a_2^2+n^2}}{n_0\sqrt{a_2^2+n_0^2}}$.	$1-\gamma e^{-a_3t}$	$\frac{n\sqrt{a_2^2+n^2}}{n_0\sqrt{a_2^2+n_0^2}}$.
t (min.).	$a_3=0{\cdot}055$.	$\frac{n_0}{2\pi}=16{\cdot}8$.	$a_3=0{\cdot}055$.	$\frac{n_0}{2\pi}=15{\cdot}6$.	$_3=0{\cdot}04$. $\gamma=0{\cdot}36$.	$\frac{n_0}{2\pi}=14{\cdot}7$.
5	0·24	—	0·24	0·43	0·71	0·71
10	0·42	0·48	0·42	0·53	0·76	0·76
15	0·56	0·64	0·56	0·63	0·80	0·79
25	0·75	0·77	0·75	0·78	0·87	0·88
35	0·85	0·88	0·85	0·82	0·91	0·92
50	0·94	0·94	0·94	0·93	0·95	0·97
70	0·98	0·95	0·98	0·98	0·98	0·98
90	0·99	0·99	0·99	0·99	0·99	1·00

and 589 equal to 0·055 and for $\lambda=670·8$ to 0·04. This first theoretical case therefore is in contradiction with experiment.

TABLE II.

		$\lambda = 510·5\ \mu\mu$.	$\lambda = 589\ \mu\mu$.	$\lambda = 670·8\ \mu\mu$.
	$1-e^{-a_3t}$.	$\frac{(n-n_1)\sqrt{a_2^2+n^2}}{(n_0-n_1)\sqrt{a_2^2+n_0^2}}$.	$\frac{(n-n_1)\sqrt{a_2^2+n^2}}{(n_0-n_1)\sqrt{a_2^2+n_0^2}}$.	$\frac{(n-n_1)\sqrt{a_2^2+n^2}}{(n_0-n_1)\sqrt{a_2^2+n_0^2}}$.
t (min.).	$a_3=0·055$.	$\frac{n_1}{2\pi}=5$; $\frac{n_0}{2\pi}=16·8$.	$\frac{n_1}{2\pi}=3$; $\frac{n_0}{2\pi}=15·6$.	$\frac{n_1}{2\pi}=10·3$; $\frac{n_0}{2\pi}=14·7$.
5	0·24	—	0·36	0·39
10	0·42	0·42	0·46	0·49
15	0·56	0·60	0·58	0·56
25	0·75	0·74	0·74	0·74
35	0·85	0·86	0·78	0·84
50	0·94	0·92	0·91	0·94
70	0·98	0·95	0·97	0·95
90	0·99	0·99	0·99	1·00

We see that in this case c_3 remains constant, and therefore the above formula gives us a good agreement with experiment.

TABLE III. .

		$\lambda = 510·5\ \mu\mu$.	$\lambda = 589\ \mu\mu$.	$\lambda = 670·8\ \mu\mu$.
	$(1-e^{-a_3t})$.	$\frac{e^{pn}}{e^{pn_0}}$.	$\frac{e^{pn}}{e^{pn_0}}$.	$\frac{e^{pn}}{e^{pn_0}}$.
t (min.).	$a_3=0·045$.	$2\pi p=0·2$; $\frac{n_0}{2\pi}=16·7$.	$2\pi p=0·22$; $\frac{n_0}{2\pi}=15·6$.	$2\pi p=0·48$; $\frac{n_0}{2\pi}=14·7$
5	0·20	—	0·31	0·33
10	0·36	0·35	0·39	0·41
15	0·49	0·51	0·50	0·46
25	0·67	0·67	0·67	0·66
35	0·79	0·82	0·72	0·76
50	0·90	0·91	0·88	0·91
70	0·96	0·94	0·96	0·93
90	0·98	1·01	0·98	0·99

TABLE IV.

		$\lambda = 510{\cdot}5\ \mu\mu$.	$\lambda = 589\ \mu\mu$.	$\lambda = 670{\cdot}8\ \mu\mu$.
	$1-e^{-a_3 t}$.	$\dfrac{e^{pn}\sqrt{a_2^2+n^2}}{e^{pn_0}\sqrt{a_2^2+n_0^2}}$.	$\dfrac{e^{pn}\sqrt{a_2^2+n^2}}{e^{pn_0}\sqrt{a_2^2+n_0^2}}$.	$\dfrac{e^{pn}\sqrt{a_2^2+n^2}}{e^{pn_0}\sqrt{a_2^2+n_0^2}}$
t (min.).	$a_3=0{\cdot}045$.	$2\pi p=0{\cdot}15$; $\frac{n_0}{2\pi}=16{\cdot}7$.	$2\pi p=0{\cdot}15$; $\frac{n_0}{2\pi}=15{\cdot}6$.	$2\pi p=0{\cdot}4$; $\frac{n_0}{2\pi}=14{\cdot}7$.
5	0·20	—	0·30	0·33
10	0·36	0·32	0·38	0·41
15	0·49	0·49	0·50	0·47
25	0·67	0·66	0·67	0·65
35	0·79	0·81	0·72	0·77
50	0·90	0·90	0·88	0·91
70	0·96	0·93	0·96	0·93
90	0·98	1·01	0·98	1·01

We see from these tables that with the formulæ

$$\frac{(n-n_1)\sqrt{\alpha_2^2+n^2}}{(n_0-n_1)\sqrt{\alpha_2^2+n_0^2}} = 1-e^{-a_3 t}, \quad \frac{e^{pn}\sqrt{\alpha_2^2+n^2}}{e^{pn_0}\sqrt{\alpha_2^2+n_0^2}} = 1-e^{-a_3 t},$$

and

$$\frac{\epsilon^{pn}}{\epsilon^{pn_0}} = 1-e^{-a_3 t}$$

we obtain a good agreement with the experimental results, the formula

$$\frac{n\sqrt{\alpha_2^2+n^2}}{n_0\sqrt{\alpha_2^2+n_0^2}} = 1-e^{-a_3 t}$$

being in contradiction with Schaternikoff's experiments, because α_3 changes for different wave-lengths. We conclude from this that formulæ 12 (b, c, d) can be used to express the law of the phenomena of flickers. In order to decide which of these three formulæ (b, c, or d) expresses the actual relations, we can test the equations 12 (b and d) by comparing with Allen's experiments. The formula (12, c) is a generalization of Allen's empirical formula and for constant adaptation gives the same relation between n and J as Allen's original formula, which is in good agreement with experiment. We need therefore to test only the formulæ 12 (b) and 12 (d).

In Tables V. and VI. we give for three wave-lengths $\lambda = 520\ \mu u$, $\lambda = 590\ \mu\mu$, and $\lambda = 665\ \mu\mu$ the values of J observed and J calculated from the formula

$$J = \sqrt{a_2^2 + n^2}\,.\,(n - n_1)\,B$$

(B is a constant; Table V.), and from the formula

$$J = \sqrt{a_2^2 + n^2}\,.\,e^{p(n-c)} \text{ (Table VI.).}$$

TABLE V.

$\lambda = 590\ \mu\mu.$

$\frac{n}{2\pi}$.	J (obs.).	$J = 0{\cdot}00093\left(\frac{n}{2\pi} - 50\right)\sqrt{a_2^2 + n^2}$.
65·36	1·000	0·93
64·52	0·883	0·873
61·73	0·587	0·672
56·18	0·250	0·323
51·02	0·117	0·048
42·02	0·030	negative value of J.
33·03	0·0076	
27·32	0·0022	
25·19	0·0010	
23·04	0·0007	

We see from this, that the first formula proposed by myself is in contradiction with Allen's data (fig. 1)

Fig. 1.

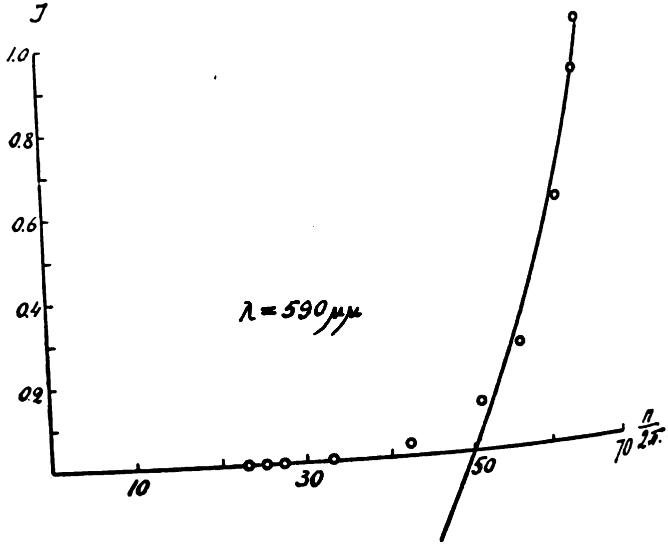


TABLE VI.

$\lambda = 520\ \mu\mu$.			$\lambda = 590\ \mu\mu$.			$\lambda = 665\ \mu\mu$.		
		$J=\sqrt{a_2^2+n^2}.e^{p(n-c)}$ $2\pi p= 0{\cdot}1485$.			$J=\sqrt{a_2^2+n^2}.e^{p(n-c)}$ $2\pi p= 0{\cdot}1306$.			$J=\sqrt{a_2^2+n^2}.e^{p(n-c)}$ $2\pi p= 0{\cdot}1248$.
$\frac{n}{2\pi}$.	J (obs.).	$\frac{c}{2\pi}=85{\cdot}0$.	$\frac{n}{2\pi}$.	J (obs.).	$\frac{c}{2\pi}=79{\cdot}73$.	$\frac{n}{2\pi}$.	J (obs.).	$\frac{c}{2\pi}=85{\cdot}3$.
59·17	1·000	1·276	65·36	1·000	1·000	54·35	1·000	1·008
57·55	0·883	0·974	64·52	0·883	0·885	53·48	0·883	0·890
54·39	0·587	0·574	61·73	0·587	0·588	50·50	0·587	0·579
49 50	0·250	0·254	56·18	0·250	0·259	44·64	0·250	0·246
44·64	0·117	0·111	51 02	0·117	0·120	39·84	0·117	0·121
37 31	0·030	0 031	42·02	0·030	0·030	30·56	0·030	0·030
29·41	0 0076	0·0076	33·03	0·0076	0 0074	22·03	0·0076	0·0072
24·09	0·0022	0·0028	27·32	0·0022	0 0029	16·00	0·0022	0·0025
21·41	0·0010	0·0017	25·19	0·0010	0·0020	12·19	0·0010	0·0012
			23·04	0·0007	0·0014			

Fig. 2.

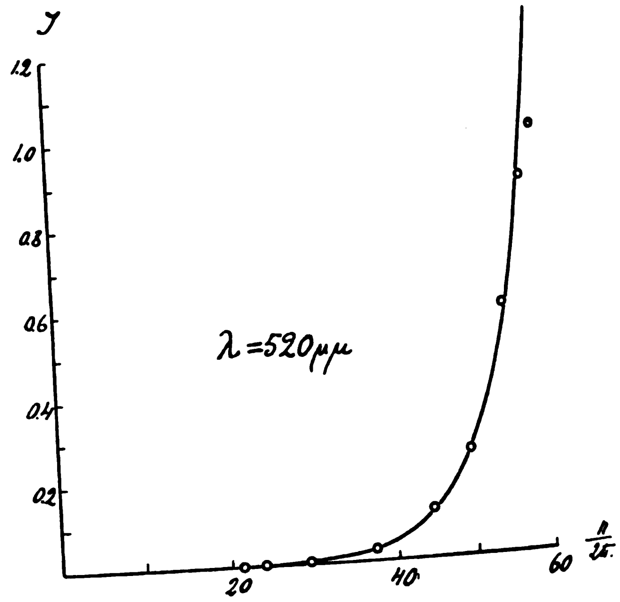
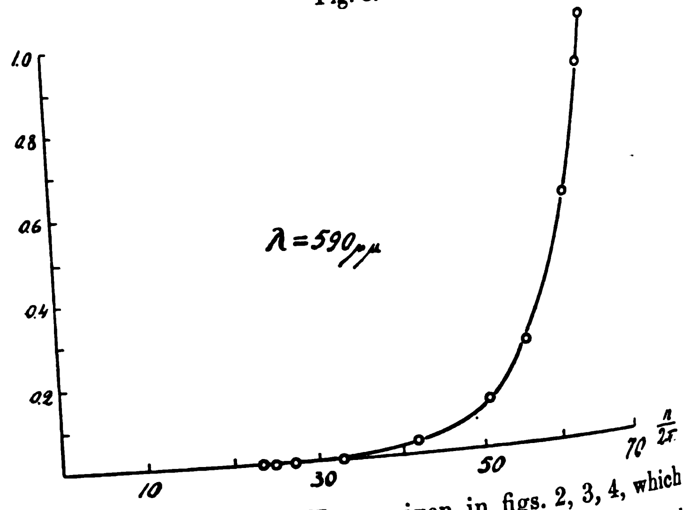


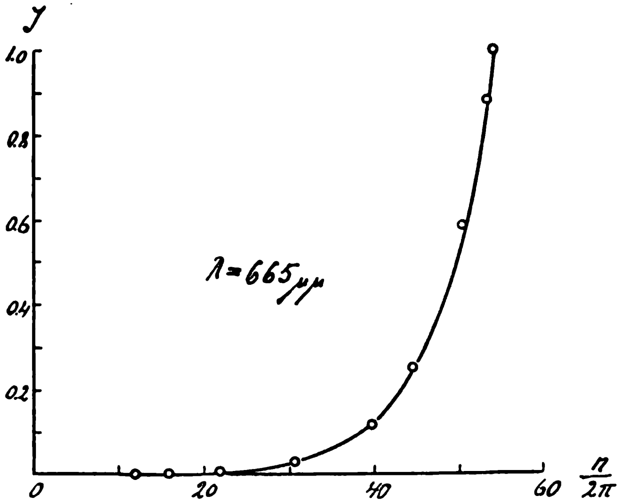
Fig. 3.



The results of Table VI. are given in figs. 2, 3, 4, which represent the relation between $\frac{n}{2\pi}$ and J (obs.) (circles) and

J calculated (continuous line), (abscissæ are $\frac{n}{2\pi}$). We see that the formula (12, d) gives very good agreement with the experiments of Allen.

Fig. 4.



From what has been said above we may conclude that the formulæ determining the threshold of continuous sensation during the action of flickering light which are in best agreement with Allen's and Schaternikoff's experimental results have the form

$$e^{pn} = \frac{1}{R}\alpha_1 k J_0 C_0 (1-\gamma e^{-a_3 t})$$

and

$$e^{pn}\sqrt{o_2^2+n^2} = \frac{1}{R}\sigma_1 k J_0 C_0 (1-\gamma e^{-a_3 t}).$$

It is impossible now to decide which of these formulæ—the generalized formula of Allen or the third formula of Lasareff—is in better agreement with experiment.

The importance of the study of flickers suggests the further investigation of this region of science, and experiments with the phenomena of flickers are being pursued in my Institute.

Moscow, Institute of Physics
and Biophysics,
3 Miusskaja, 3.

CXII. *The Legendre Function of Order* $-\frac{1}{2}$.

By H. V. LOWRY *.

1. THE Legendre function of order $-\frac{1}{2}$ is the solution of

$$(1-x^2)\frac{d^2y}{dx^2}-2x\frac{dy}{dx}-\frac{1}{4}y=0, \quad . \quad . \quad . \quad (1)$$

which equals 1 when $x=1$.

The solution regular near $x=1$ satisfying this condition is

$$\mathrm{F}\left(\frac{1}{2},\ \frac{1}{2},\ 1,\ \frac{1-x}{2}\right).$$

The general solution regular near $x=\infty$ is

$$x^{-\frac{1}{2}}[(\mathrm{A}+\mathrm{B}\log x)\mathrm{K}(x)+\mathrm{BI}(x)], \quad . \quad . \quad . \quad (2)$$

where

$$\mathrm{K}(x)=1+\frac{1\,.\,3}{4^2}\frac{1}{x^2}+\frac{1\,.\,3\,.\,5\,.\,7}{4^2\,.\,8^2}\frac{1}{x^4}+\ldots\ldots$$

and

$$\mathrm{I}(x)=2\left[\frac{1\,.\,3}{4^2}\left(\frac{1}{3}\right)\frac{1}{x^2}+\frac{1\,.\,3\,.\,5\,.\,7}{4^2\,.\,8^2}\left(\frac{1}{3}+\frac{1}{5}+\frac{1}{7}-\frac{1}{2}\right)\frac{1}{x^4}+\ \ldots\right].$$

Putting $\qquad x=\dfrac{t^{\frac{1}{2}}+t^{-\frac{1}{2}}}{2}$ and $y=t^{\frac{1}{4}}w$,

(1) becomes

$$t(1-t)\frac{d^2w}{dt^2}+(1-2t)\frac{dw}{dt}-\frac{1}{4}w=0.$$

Hence

$$\mathrm{P}_{-\frac{1}{2}}(x)=\mathrm{F}\left(\frac{1}{2},\ \frac{1}{2},\ 1,\ \frac{1-x}{2}\right)=t^{\frac{1}{4}}\mathrm{F}\left(\frac{1}{2},\ \frac{1}{2},\ 1,\ 1-t\right). \quad (3)$$

Using the analytical continuation of $\mathrm{F}(\frac{1}{2},\ \frac{1}{2},\ 1,\ 1-t)$, regular near $t=0$, which is given in Forsyth's 'Theory of Differential Equations,' pt. 3, p. 130,

$$\begin{aligned}\mathrm{P}_{-\frac{1}{2}}(x)=\frac{2}{\pi}t^{\frac{1}{4}}\Bigg[&\left(2\log 2-\frac{1}{2}t\right)\mathrm{F}\left(\frac{1}{2},\ \frac{1}{2},\ 1,\ t\right)\\ &-\left\{\left(\frac{1}{2}\right)^2t+\left(\frac{1\,.\,3}{2\,.\,4}\right)^2\left(1+\frac{2}{3\,.\,4}\right)t^2+\left(\frac{1\,.\,3\,.\,5}{2\,.\,4\,.\,6}\right)^2\right.\\ &\left.\left(1+\frac{2}{3\,.\,4}+\frac{2}{5\,.\,6}\right)t^3+\ldots\right\}\Bigg]. \quad . \quad . \quad . \quad (4)\end{aligned}$$

Comparing (2) and (4) when $t\rightarrow 0$,

$$\mathrm{A}=\frac{\sqrt{2}}{\pi}(3\log 2)\ \text{and}\ \mathrm{B}=\frac{\pi}{\sqrt{2}}.$$

---

* Communicated by the Author.

2. The quarter period K of the Jacobian Elliptic Function of modulus k is

$$\frac{\pi}{2}\mathrm{F}\left(\frac{1}{2},\,\frac{1}{2},\,1,\,k^2\right)=\frac{\pi}{2k'}\mathrm{F}\left(\frac{1}{2},\,\frac{1}{2},\,1,\,\frac{k^2}{k^2-1}\right). \quad . \quad (5)$$

Identifying the last form in (5) with $\mathrm{F}\left(\frac{1}{2},\,\frac{1}{2},\,1,\,\frac{1-x}{2}\right)$,

$$x=\frac{1+k^2}{1-k^2} \text{ and } t=\left(\frac{1-k}{1+k}\right)^2.$$

Hence

$$\mathrm{K}=\frac{\pi}{2k'}\left(\frac{1-k}{1+k}\right)^{-\frac{1}{2}}\mathrm{P}_{-\frac{1}{2}}\left(\frac{1+k^2}{1-k^2}\right)$$

$$=\frac{\pi}{2}\,\frac{1}{1-k}\mathrm{F}\left(\frac{1}{2},\,\frac{1}{2},\,1,\,\frac{4k}{(1+k)^2}\right),$$

which by (4)

$$=\frac{1}{1-k}\left[\left(2\log 2-\log\left(\frac{1-k}{1+k}\right)\right)\mathrm{F}\left\{\frac{1}{2},\,\frac{1}{2},\,1,\,\left(\frac{1-k^2}{1+k^2}\right)\right\}\right.$$

$$\left.-\left\{\left(\frac{1}{2}\right)^2\left(\frac{1-k}{1+k}\right)^2+\left(\frac{1\,.\,3}{2\,.\,4}\right)^2\left(1+\frac{2}{3\,.\,4}\right)\left(\frac{1-k}{1+k}\right)^4+\ldots\right\}\right].$$

The last form is suitable for calculating K when k is nearly 1.

By identifying each of the forms in (5) with

$$\mathrm{F}\left(\frac{1}{2},\,\frac{1}{2},\,1,\,\frac{1-x}{2}\right) \text{ and } \mathrm{F}\left(\frac{1}{2},\,\frac{1}{2},\,1,\,1-t\right),$$

we obtain various transformations of K corresponding to the quadratic transformations of the elliptic integrals.

3. Since

$$\left.\begin{aligned}\mathrm{P}_{-\frac{1}{2}}(x)&=\mathrm{F}\left(\frac{1}{2},\,\frac{1}{2},\,1,\,\frac{1-x}{2}\right)\\ \mathrm{P}'_{-\frac{1}{2}}(x)&=-\frac{1}{8}\mathrm{F}\left(\frac{3}{2},\,\frac{3}{2},\,2,\,\frac{1-x}{2}\right)\end{aligned}\right\}. \quad . \quad . \quad (6)$$

Differentiating (1), we find $\mathrm{P}'_{-\frac{1}{2}}(x)$ satisfies

$$(1-x^2)\frac{d^2y}{dx^2}-4x\frac{dy}{dx}-\frac{9}{4}y=0 \quad . \quad . \quad (7)$$

Putting $x = \dfrac{t^{\frac{1}{4}} + t^{-\frac{1}{4}}}{2}$ and $y = t^{\frac{3}{4}} w$,

(6) becomes

$$t(1-t)\frac{d^2w}{dt^2} + (1-4t)\frac{dw}{dt} - \frac{9}{4}y = 0.$$

Hence $$\mathrm{P}'_{-\frac{1}{2}}(x) = -\frac{1}{8}t^{\frac{3}{4}}\mathrm{F}\left(\frac{3}{2}, \frac{3}{2}, 3, 1-t\right). \quad . \quad . \quad (8)$$

The general solution of (7) regular near $x = \infty$ is

$$x^{-\frac{3}{2}}\left[(\mathrm{A}' + \mathrm{B}'\log x)\mathrm{K}_1(x) + \mathrm{B}'\mathrm{I}_1(x)\right], \quad . \quad . \quad (9)$$

where $$\mathrm{K}_1(x) = 1 + \frac{3\,.\,5}{4^2}\frac{1}{x^2} + \frac{3\,.\,5\,.\,7\,.\,9}{4^2\,.\,8^2}\frac{1}{x^4} + \ldots.$$

and $$\mathrm{I}_1(x) = 2\left\{\frac{3\,.\,5}{4^2}\left(\frac{1}{3} + \frac{1}{5} - \frac{1}{2}\right)\frac{1}{x^2} + \frac{3\,.\,5\,.\,7\,.\,9}{4^2 8^2}\left(\frac{1}{3} + \frac{1}{5} + \frac{1}{7} + \frac{1}{9} - \frac{1}{2} - \frac{1}{4}\right)\frac{1}{x^4} + \ldots\right\}.$$

But when x is very large, we have from (2)

$$\mathrm{P}'_{-\frac{1}{2}}(x) = x^{-\frac{3}{2}}\{\mathrm{B} - \tfrac{1}{2}(\mathrm{A} + \mathrm{B}\log x)\} \text{ nearly.}$$

Hence $$\mathrm{A}' = -\frac{\mathrm{A}}{2} + \mathrm{B} = -\frac{\sqrt{2}}{2\pi}(3\log 2 - 2)$$

nd $$\mathrm{B}' = -\frac{\sqrt{2}}{\pi}.$$

The corresponding solution regular near $t = 0$ is

$$-\frac{t^{\frac{3}{4}}}{\pi}\left[(4\log 2 - 4 - \log t)\,\mathrm{F}\left(\frac{3}{2}, \frac{3}{2}, 1, t\right) - 4\left\{\left(\frac{3}{2}\right)^2\left(\frac{1}{3} - \frac{1}{2}\right)t + \frac{\left(\frac{3}{2}\right)^2\cdot\left(\frac{5}{2}\right)^2}{2}\left(\frac{1}{3} + \frac{1}{5} - \frac{1}{2} - \frac{1}{4}\right)t^2 + \ldots\right\}\right]. \quad . \quad (10)$$

4. The mutual inductance of two parallel circular coaxial circuits radii a, A, and d apart is

$$\mathrm{M} = \int_0^{\pi}\frac{4\pi\mathrm{A}a\cos\theta\,d\theta}{\sqrt{\mathrm{A}^2 + a^2 + d^2 - 2\mathrm{A}a\cos\theta}}$$

$$= \int_0^{\pi}\frac{\pi(r_1{}^2 - r_2{}^2)}{(r_1 r_2)^{\frac{1}{2}}}\,\frac{\cos\theta\,d\theta}{\sqrt{x - (x^2-1)^{\frac{1}{2}}\cos\theta}},$$

where $$r_1^2=(A+a)^2+d^2,$$
$$r_2^2=(A-a)^2+d^2,$$

and $$x=\frac{r_1^2+r_2^2}{2r_1r_2},\ t=\left(\frac{r_2}{r_1}\right)^2 \text{ or } \left(\frac{r_1}{r_2}\right)^2.$$

Hence

$$M=-\frac{\pi(r_1^2-r_2^2)}{(r_1r_2)^{\frac{1}{2}}}(x^2-1)^{\frac{1}{2}}\frac{d}{dx}\int_0^\pi \sqrt{x-(x^2-1)^{\frac{1}{2}}\cos\theta}\,d\theta$$
$$=-\frac{\pi(r_1^2-r_2^2)^2}{2(r_1r_2)^{\frac{3}{2}}}\frac{d}{dx}\{2\pi P_{-\frac{1}{2}}(x)\}$$
$$=-\frac{\pi^2(r_1^2-r_2^2)^2}{(r_1r_2)^{\frac{3}{2}}}P'_{-\frac{1}{2}}(x).$$

Using the forms of $P'_{-\frac{1}{2}}(x)$ given in (6), (8), (9), and (10), we have

$$M=\frac{\pi^2}{8}\frac{(r_1^2-r_2^2)^2}{(r_1r_2)^{\frac{3}{2}}}F\left(\frac{3}{2},\frac{3}{2},2,-\frac{(r_1-r_2)^2}{4r_1r_2}\right) \quad . \quad . \quad . \quad . \quad (11)$$
$$=\frac{\pi^2}{8}\frac{(r_1^2-r_2^2)^2}{r_1^3}F\left(\frac{3}{2},\frac{3}{2},3,\frac{r_1^2-r_2^2}{r_1^2}\right) \quad . \quad . \quad . \quad . \quad . \quad (12)$$
$$=\frac{2\pi(r_1^2-r_2^2)^2}{(r_1^2+r_2^2)^{\frac{3}{2}}}[(3\log 2-2+\log x)K_1(x)+I_1(x)] \, . \quad (13)$$
$$=\frac{2\pi(r_1^2-r_2^2)^2}{r_1^3}\Bigg[(4\log 2-4-\log t)\,F\left(\frac{3}{2},\frac{3}{2},1,t\right)$$
$$-4\left\{\left(\frac{3}{2}\right)^2\left(\frac{1}{3}-\frac{1}{2}\right)t+\left(\frac{3}{2}\right)^2\left(\frac{5}{2}\right)^2\frac{1}{2^2}\left(\frac{1}{3}+\frac{1}{5}-\frac{1}{2}-\frac{1}{4}\right)t^2\right.$$
$$\left.+\ldots\right\} . \quad . \quad (14)$$

(12) and (14) are formulæ given by Maxwell.

By using a hypergeometric transformation, (11) becomes

$$M=\frac{\pi^2(r_1-r_2)^2}{r_1+r_2}F\left(\frac{3}{2},\frac{1}{2},2,\left(\frac{r_1-r_2}{r_1+r_2}\right)^2\right), \quad . \quad (15)$$

another formula given by Maxwell.

CXIII. *The Thermoelectric Properties of Certain Metallic Solid Solutions.* *By* A. L. NORBURY, *D.Sc.* (*University College, Swansea*) *.

CONTENTS.

1. Determination of E.M.Fs. set up at temperatures between −191° and 500° C. by certain copper alpha solid solution alloys when coupled against copper.
2. Comparison of effects of equiatomic quantities of elements in solid solution on the thermoelectric properties of copper and certain other metals.
3. A new type of thermoelectric formula.

1. DETERMINATION OF E.M.Fs. SET UP AT TEMPERATURES BETWEEN — 191° AND 500° C. BY CERTAIN COPPER ALPHA SOLID SOLUTIONS WHEN COUPLED AGAINST COPPER.

THE alloys used were in the form of wires (0·03 inch diam.). Their compositions are given in Table I.; their preparation etc. is described in previous papers †; they were annealed at a red heat by passing them through a bunsen burner.

The E.M.Fs. set up by these alloys at various temperatures against a H.C. copper wire (0·03 inch diameter, 101·6 per cent. conductivity) were measured with a Tinsley Vernier Potentiometer reading to 1 microvolt.

The cold junctions were maintained throughout at 16° C. in a thermos flask. The hot junctions were fused (using borax) for the higher temperatures; for the lower temperatures, satisfactory junctions were made by plugging the cleaned ends of the wires into a small piece of copper tubing.

In order to obtain reliable results it was found very necessary—owing to heat conduction—to have several inches of the couple immersed in a constant-temperature medium.

This was effected by placing the hot junctions of the couples in glass tubes—closed at one end—which were immersed to a depth of about nine inches in the vapours generated by boiling ethyl alcohol (78°), water (100°), aniline (183°), and napthalene (218° C.) in 5-litre flasks, and by boiling mercury (356°) and sulphur ‡ (444° C.)

---

* Communicated by the Author.

† 'Journal of the Institute of Metals,' xxix. p. 423 (1923); xxxiii. p. 91 (1925)

‡ The temperature of the glass tubes in this thermostat was constant at 438° vice 444°. The difference was probably due to liquid sulphur condensing and running down the tubes.

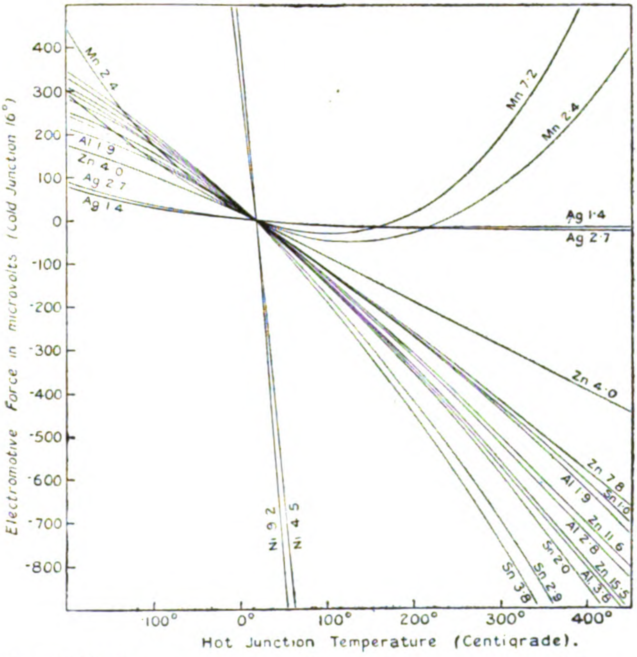
(the latter in an atmosphere of nitrogen) in four-inch internal diameter steel tubes.

For the temperatures below 0° C., Dewar flasks containing liquid air (−191°), and alcohol cooled with solid carbon dioxide (0° to −78°) were used. In the latter range, the temperatures were taken with a pentane thermometer, calibrated in liquid air (assumed to be −191°), solid carbon dioxide (−78°), and ice (0° C.). For temperatures above 444° the hot junctions were placed in silica tubes immersed to a depth of about nine inches in an electrically heated bath of molten lead.

Every time an E.M.F. measurement was made, the temperature of the thermostat in question was checked by means of a calibrated Pt–Pt, Rh thermocouple, which was placed in the thermostat in a similar tube to that containing the couple under measurement.

Fig. 1.

E.M.Fs. set up against Copper by Certain Copper Alpha Solid Solution Alloys.



The E.M.Fs. set up by the various copper alpha solid solutions when coupled against copper at temperatures between −191° and 500° C. are given in Table I. and plotted in fig. 1.

TABLE I.

E.M.Fs. set up against Copper at Temperatures between −200° and 500° C. by Certain Copper Alpha Solid Solution Alloys.

ADDED ELEMENT.		ELECTROMOTIVE FORCE (microvolts) AGAINST COPPER (Cold Junction 16° C.)													
Weight %.	Atomic %.	(−200°).	−191°.	(−100°).	(0°).	78°.	100°.	183°.	(200°).	218°.	(300°).	356°.	(400°).	438°.	(500°).
Al 1·92	Al 4·39	217	210	132	20	−86	−116	—	−271	−300	−442	−547	−629	−703	−827
Al 2·88	Al 6·52	315	304	184	30	−108	−144	—	−319	−354	−517	−637	−730	−809	−943
Al 3·82	Al 8·53	346	333	201	32	−117	−163	—	−355	−393	−574	−703	−805	−892	−943
Mn 2·40	Mn 2·77	443	409	174	19	− 43	− 50	−28	− 25	− 11	83	170	273	368	—
Mn 7·20	Mn 8·25	288	271	139	13	− 25	− 25	—	20	39	198	363	632	701	—
Ni 4·52	Ni 4·88	2580	2515	−1720	300	−1209	−1664	−3590	−4120	−4589	−6870	−8539	−9920	−11148	—
Ni 9·20	Ni 9·89	3210	3124	2100	390	−1512	−2101	−4639	−5230	−5576	−8710	—	−12954	−14833	—
Zn 4·06	Zn 3·96	175	168	100	14	− 60	− 84	—	−186	−206	−289	−345	−393	−433	−500
Zn 7·86	Zn 7·66	221	214	135	20	− 88	−118	—	−261	−289	−415	−510	−585	−646	−753
Zn 11·66	Zn 11·36	256	248	155	24	−103	−138	—	−311	−348	−502	−615	−704	−784	−906
Zn 15·58	Zn 15·19	284	275	174	26	−108	−176	—	−341	−379	−562	−695	−794	−881	—
Ag 1·44	Ag 0·85	73	65	25	2	− 6	− 7	—	− 14	− 17	− 18	− 19	− 19	− 20	−20
Ag 2·75	Ag 1·64	88	80	30	3	− 7	− 8	—	− 16	− 19	− 20	− 21	− 21	− 22	−22
Sn 1·00	Sn 0·54	244	235	145	24	−88	−118	−244	−269	−299	−431	−531	−610	−680	−794
Sn 2·03	Sn 1·10	301	289	177	29	−115	−157	−322	−358	−392	−596	−738	−854	−956	—
Sn 2·96	Sn 1·60	334	321	192	30	−129	−178	−378	−419	−465	−701	−882	−1030	−1173	—
Sn 3·88	Sn 2·11	348	334	201	32	−138	−191	−407	−457	−503	−756	−945	−1100	−1235	—

(The E.M.F. values below the temperatures shown in brackets have been estimated by interpolation.)

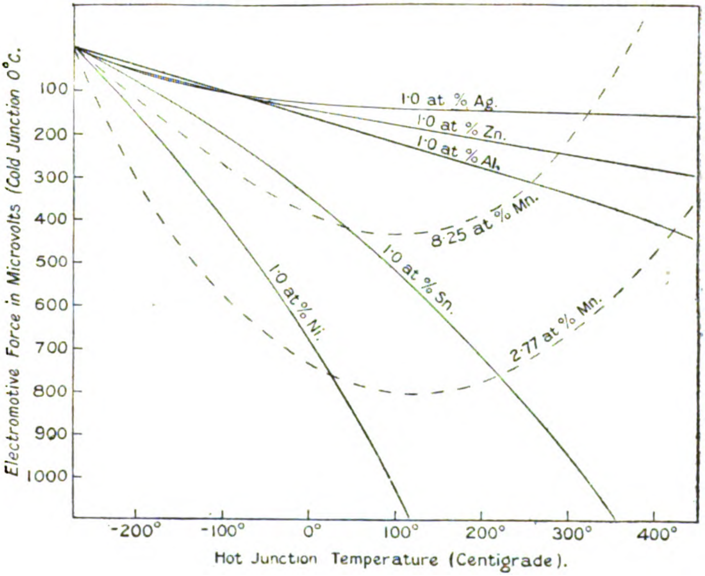
It will be seen in fig. 1 that the curves for most of the alloys are relatively simple and similar in nature. Those for the manganese-copper alloys are, however, of a different type from any of the others. The fact that manganese-copper alloys give small E.M.Fs. against copper round about room temperatures is clearly shown.

2. COMPARISON OF EFFECTS OF EQUIATOMIC QUANTITIES OF ELEMENTS IN SOLID SOLUTION ON THE THERMOELECTRIC PROPERTIES OF CERTAIN METALS.

In order to compare the atomic effect of one solute element with the atomic effect of another solute element on the thermoelectric properties of copper, the curves in fig. 2 have been constructed by interpolation.

Fig. 2.

E.M.Fs. (calculated) that Copper Solid Solutions (each containing 1·0 atomic per cent. Added Element) would set up against Copper at various Temperatures if the Cold Junction was at −273° C.

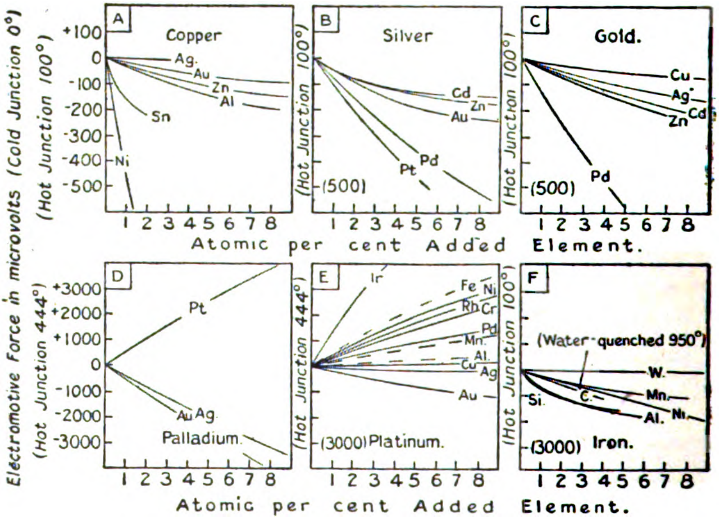


They show the E.M.Fs. that would be set up if copper alloys—each containing 1·0 atomic per cent. added element in solid solution—were coupled against copper at the temperatures indicated. A second simplification has been introduced by constructing the curves for a cold junction temperature of $-273°$, the necessary data being obtained by extrapolation. It has not been possible to construct a 1·0 atomic per cent. curve for manganese owing to this element's complicated effect. The curves for the two manganese alloys available have, however, been dotted-in in fig. 2.

Fig. 3.

E.M.Fs. set up by :—

A. Copper Solid Solutions against Copper at 100° C.
B. Silver " " " Silver " "
C. Gold " " " Gold " "
D. Palladium " " " Palladium at 444° C.
E. Platinum " " " Platinum " "
F. Iron " " " Iron at 100° C.



It is suggestive that the order of the atomic effects in fig. 1,—viz. Ag, Zn, Al, Sn, Ni,—is the same as the order of these elements in the Periodic Table, reading from Ag in Group 1 to Ni in Group 8.

In order to find out if this type of relationship occurs in other solid solutions, the curves in figs. 3 (A–F) and 4 have been constructed from the data published by previous investigators [*].

Owing to the nature of the data available it has only been possible to plot E M.F. against atomic per cent. added element for a single temperature in each case; but a study of figures 1 and 2 indicates that this should give—except in exceptional cases like the manganese-copper alloys—a general idea of the relative atomic effects of the solute elements.

In figs. 3 A, 3 B, and 3 C it will be seen that the silver and gold solid solutions are similar to the copper solid in that the solute elements in Groups 1 and 2 have small electronegative effects and those in Group 8 large electronegative effects.

Considering now the palladium and platinum solid solutions in figs. 3 D and 3 E, it will be seen that Cu, Ag, and Au (Group 1) have electronegative effects (Cu in Pt has a small electropositive effect), while the elements in Group 8 have electropositive effects. The order of the solute elements is similar to that in figs. 3 A, 3 B, 3 C, but inverted.

Fig. 3 F shows iron solid solutions. The elements C, Mn, Ni, and W probably have complex effects in that they also cause an allotropic change to take place in the solvent metal, and the water-quenched carbon-iron alloys—although included in this figure—are not true solid solutions. The Al and Si curves should, however, be fairly representative.

The curves for the Ni solid solutions in fig. 4 have been constructed in a similar manner to those in fig. 2, only they represent 5·0 atomic per cent. alloys, since for one or two of the solute elements only one alloy of approximately this composition was tested.

It will be seen that Cu has an electronegative effect recalling the effects of Ag and Au on Pd and Pt in figs. 3 D and 3 E (since Ni, Pd, and Pt are all in Group 8 *c*).

---

[*] These figures have been constructed from data as follows:—

3 A. From Table I. and from Sedström, *Annalen der Physik*, lix. (4) p. 134 (1919).

3 B. From Sedström, *loc. cit.*, and from Geibel, *Zeit. für Anorg. Chem.* lxix. p. 38 (1910), lxx. p. 240 (1911).

3 C. From Sedström and Geibel, *loc. cit.*

3 D. From Geibel, *loc. cit.*

3 E. From Geibel, *loc. cit.*, and Barus, Bull. U.S. Geol. Survey, 1889, Nos. 54 and 103.

3 F. From Dupuy and Portevin, Journ. Iron and Steel Inst. 1915 (1) p. 306.

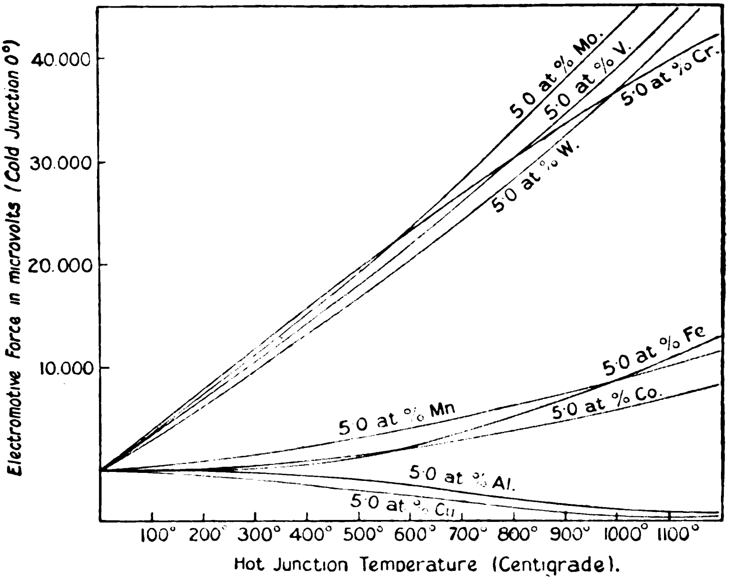
4. From Robin, *Zeit. für Metallkunde*, Aug. 1924, p. 297, and from 'The Measurement of High Temperatures,' by Le Chatelier and Burgess, 1912, p. 171.

The curves for several of the other solute elements in fig. 4 are somewhat complicated and cross one another.

In general, a consideration of the foregoing figures suggests that there is a connexion—provided complications do not occur—between the effect of a solute element on the thermoelectric properties of a metallic solvent and the positions of the solute and solvent elements in the Periodic Table.

Fig. 4.

E.M.Fs. set up against Nickel by Nickel Alpha Solid Solutions (each containing 5·0 atomic per cent. Added Element) at Temperatures between 0° and 1200°.



The positions of the elements in the Periodic Table necessarily only give an approximate guide to the actual factors concerned, which are presumably connected with the effects of the solute atoms on the electrons of the solvent atoms. It is significant that the effect of a solute element on the thermoelectric properties of a metallic solvent is different from its effect on the latter's electrical resistivity *, since, in the latter case, proximity of solute and solvent in the Periodic Table—rather than position—appears to be the deciding factor.

---

* *Cf.* Norbury, Trans. Faraday Soc. xvii. p. 251 (1921), and Journ. Inst. Metals, xxxiii. p. 91 (1925).

3. A NEW TYPE OF THERMOELECTIC FORMULA.

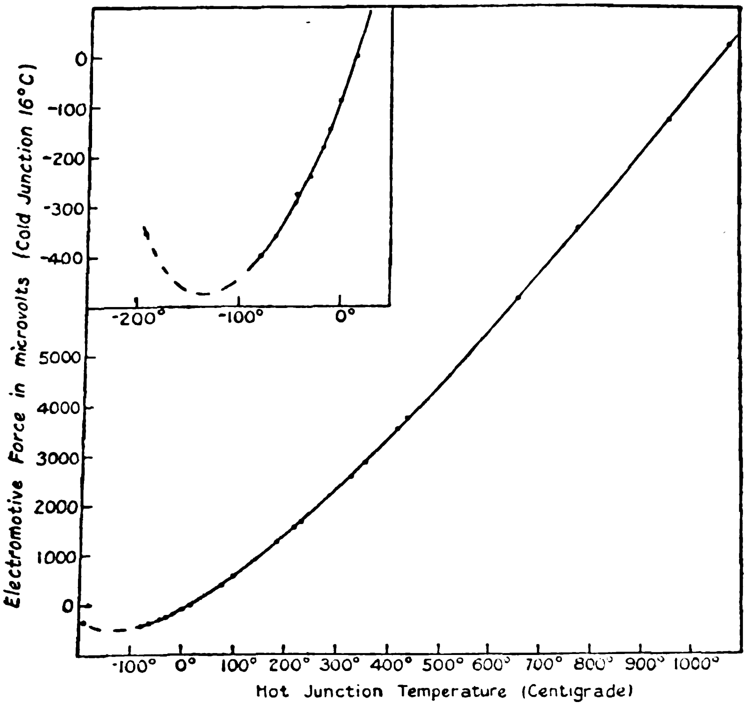
Various formulæ have been put forward from time to time for expressing the temperature–E.M.F. relationship of the platinum–platinum 90 per cent., rhodium 10 per cent. thermocouple.

The following formulæ are given by Le Chatelier and Burgess*, who discuss and compare them :—

1. $\Sigma_0^t e = mt^n$ (Holman).
2. $\Sigma_0^t e = -a + bt + ct^2$ (Holborn and Day).
3. $e = a\mathrm{T} + b \log \mathrm{T} + c$ (Stansfield).
4. $t = a + be - ce^2$.

Fig. 5.

E.M.Fs. set up at Temperatures between −191° and 1083° C. by Platinum–Platinum 90 %, Rhodium 10 % Thermocouple.



The data obtained for the Pt–Pt, Rh thermocouple used in the present experiments have been plotted in fig. 5.

---

* 'The Measurement of High Temperatures,' by Le Chatelier and Burgess, p. 114 (1912).

TABLE II.

Observed E.M.Fs. of Pt—Pt 90 %, Rh 10 % Thermocouple compared with E.M.Fs. calculated using Formulæ of the type: $\text{E.M.F.} = -a + bT + c\,.\,10^{-dT}$.

1.	2.	3.	4.	5.	6.	7.
Hot Junction Temperature. (Cold Junction, 16° C.)		E.M.F. observed. (microvolts.)	E.M.F. calculated. (Formula *a*.)[1]	Difference[3]. (Column 3 —Column 4.)	E.M.F. calculated. (Formula *b*.)[2]	Difference[3]. (Column 3 —Column 6.)
Cent.	Abs.					
−191	82	−356	−357	1	−383	27
− 78	195	−401	−393	− 8	−389	−12
− 62	211	−360	−345	−15	−342	−18
− 42	231	−292	−278	−14	−272	−20
− 29	244	−240	−227	−13	−217	−23
− 16	257	−181	−170	−11	−159	−22
− 10	263	−144	−142	−2	−132	−12
0	273	− 89	− 93	4	− 81	− 8
16	289	0	− 10	10	1	− 1
78	351	404	378	26	391	13
100	373	558	536	22	548	10
183	456	1234	1209	25	1216	18
218	491	1533	1523	10	1526	7
232	505	1650	1648	2	1654	− 4
327	600	2585	2583	2	2573	12
356	629	2874	2882	− 8	2868	6
419	692	3520	3550	−30	3527	− 7
438	711	3733	3755	−22	3729	4
658	931	6150	6232	−82	6167	−17
779	1052	7580	7650	−70	7553	27
961	1234	9750	9789	−49	9666	84
1083	1356	11240	11243	− 3	11094	146

---

[1] Formula *a*: $\text{E.M.F.} = -5{,}050 + 12{\cdot}0\,T + 5{,}210 \times 10^{-0{\cdot}0018\,T}$ microvolts.

[2] Formula *b*: $\text{E.M.F.} = -4{,}900 + 11{\cdot}8\,T + 5{,}020 \times 10^{-0{\cdot}0018\,T}$ microvolts.

[3] A difference of 1° C. causes a difference of 6 microvolts at 16° C. and 12 microvolts at 1000° C.

It will be seen that the curve passes through a minimum at about $-135°$ C. It follows, in consequence, that none of the above formulæ is of the right type to fit the curve at temperatures below $-135°$. A formula of the following type has been found to express the results closely over a wide temperature range :

$$5. \quad e = -a + bT + c \cdot 10^{-dT},$$

where T=absolute temperature of hot junction, and a, b, c, and d are constants depending on the thermocouple and on the cold junction temperature. The constants can be evaluated graphically by drawing a tangent to the high temperature end of the curve and plotting the logarithms of the E.M.F. differences between the tangent and the curve against the absolute temperatures. The latter relationship, being a linear one, gives the values of the constants c and d.

The observed E.M.F. values plotted in fig. 5 are given in Table II. column 3. Columns 4 and 6 in this table show the E.M.Fs. calculated, using formulæ of the new type (5) with slightly different values for the constants in each case.

TABLE III.

Comparison of Thermoelectric Formulæ.
(Pt–90 °/₀ Pt, 10 °/₀ Rh.)

Formulæ 1 to 4 from Le Chatelier and Burgess, *loc. cit.*
Formula 5 : $\text{E.M.F.} = -8{,}000 + 13\cdot0T + 6{,}060 \times 10^{-0\cdot00018T}$.

Substance.	Freezing Point. ° C.	E.M.F. observed. (microvolts.)	Observed Minus Calculated Temperature. Formula used.				
			1.	2.	3.	4.	5.
Cadmium	320·0	2,502	−0·2	−0·3	6·9	−1·1	−0·1
Zinc	418·2 *	3,429	0·0*	0·0*	0·0*	0·0*	−2·5*
Antimony	629·2	5,529	2·3	0·0	0·0	−0·1	−1·7
Silver............	960·0	9,111	2·5	0·2	2·2	−0·9	1·9
Gold	1062·5	10,296	0·4	0·2	0·0	0·0	1·3
Copper	1082·6	10,535	0·0	0·0	0·0	0·1	1·0
Diopside	1391	14,231	−6	10	−10	19	−0·6
Nickel	1452	14,969	−6	14	−11	28	−0·3
Cobalt	1490	15,423	−7	14	−13	31	0·6
Palladium ...	1549	16,140	−5	20	−14	42	1·2
Platinum	1755	18,613	1	42	−15	73	8·0

* The F.P. of Zn is now usually taken as 419°·4 C. This alters the differences in columns 1–5 to 1°·2, 1°·2, 1°·2, 1°·2, and −1°·3.

Columns 5 and 7 show the differences between observed and calculated values. It will be seen that the formulæ fit the results fairly accurately, since a difference of only 1° C. causes a difference of about 6 microvolts at 16° C. and about 12 microvolts at 1000° C. There are, however, certain small systematic differences which show that the formulæ are not exact.

Columns 1–7 in Table III. are reproduced from Le Chatelier and Burgess. In this table they compare the accuracy with which formulæ 1 to 4 (referred to previously) fit the experimental results of Day and Sosman. In column 8 are shown results calculated using the new type of formula. It will be seen that this formula fits the results more accurately than formulæ 1–4,—in fact, does so within the limits of experimental error. This type of formula also fits all the results plotted in fig. 1—within the limits of experimental error.

In conclusion the author wishes to acknowledge his indebtedness to Mr. R. Wilson, M.A., for suggestions with regard to the third section of the paper; to Professor C. A. Edwards, D.Sc., for facilities for carrying out the work and for his encouragement; and to the Royal Society for a Government Grant.

CXIV. *The Adsorption of Nitrogen at Low Pressures by Activated Charcoal.* *By* RUFUS CHAPLIN, *B.Sc., A.I.C.*[*]

INTRODUCTION.

THIS investigation was suggested by a consideration of the results of a preliminary study of the action of activated charcoal at ordinary temperature on traces of air. The preliminary study, undertaken in connexion with another investigation on charcoal involving vacuum technique, indicated that the nitrogen of the air is not very efficiently dealt with in a "clean-up" process carried out with a moderate amount of charcoal at ordinary temperatures. The extent to which pure nitrogen at low pressures was taken up by charcoal was therefore studied.

The experiment with nitrogen consisted in determining the 25° isotherm in the pressure region 2×10^{-4} to $1{\cdot}3 \times 10^{-2}$ mm. of Hg.

The preliminary experiments with air are also included in this paper and are described later.

[*] Communicated by the Author.

EXPERIMENTAL.

The pressures were measured on a modified form of McLeod gauge. The quantities of gas adsorbed are minute at these low pressures and had to be arrived at from a consideration of pressure changes in an apparatus of constant volume and sufficiently constant temperature, a special precaution being taken in the case of the isotherm to prevent the quantity errors from becoming cumulative (*vide* nitrogen experiments). Thus no other measurements but those of pressure were necessary, and since on these the validity of the results entirely depended, a specially designed McLeod gauge * was employed. This is described in some detail below.

Fig. 1.

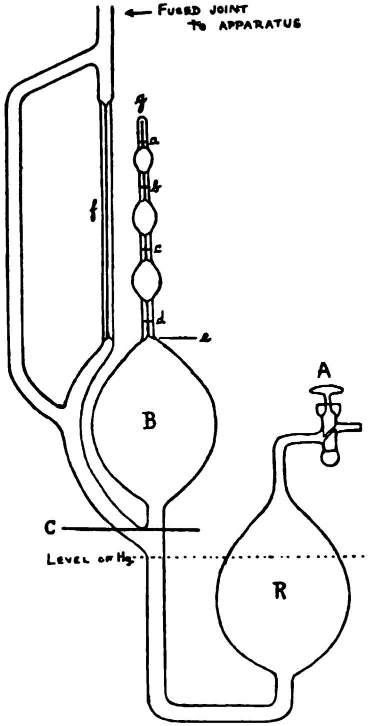


Fig. 1 shows a sketch of the gauge, which is of fused glass throughout. "R," the reservoir bulb, has a capacity of 300 c.c. and is furnished with a vacuum tap A.

---

* Due in great part to one of the author's colleagues.

The total capacity of B, including the bulbed appendix "*g*" to the cut-off level C, is 247 c.c.

"*g*" and "*f*" are cut from the same piece of 0·8 mm. capillary tubing, carefully selected for uniformity of bore.

"*f*" is 26 cm. long, "*g*" is 22 cm. long, and before fusing on at "*e*" bulbs, conveniently spaced, are blown on it as follows:—

$$\left.\begin{array}{llll}\text{upper bulb} & 0\cdot1 \text{ c.c.} & \text{capacity} \\ \text{centre} \quad ,, & 0\cdot5 \text{ c.c.} & \quad ,, \\ \text{lower} \quad ,, & 1\cdot8 \text{ c.c.} & \quad ,, \end{array}\right\} \text{(approx.).}$$

"*a*," "*b*," "*c*," "*d*" are fine scratches on the capillary. The volumes from tip of "*g*" to these scratches are accurately obtained by calibration with mercury, as is also the volume per unit length of capillary round about each scratch. "*g*" is then fused on to "B" at "*e*." The sketch shows disposition of "B" and "R."

In use "B" and "R" are evacuated alternately in stages, "B" via the apparatus by the h.v. pumps, and "R" via "A" by a Geryk hand pump. To raise the Hg in "B" a sufficient pressure of air is slowly admitted through "A" into "R." "R" is evacuated again when the mercury is to be lowered. In making a measurement the mercury is *slowly* raised up into "*g*," always being brought to rest in one of the capillaries. "*f*" and "*g*" are gently tapped, and the difference in height of the two mercury columns is read off on a cathetometer to within 0·05 mm. The distance between the mercury meniscus in "*g*" and the selected mark is similarly read off, and this measures the volume to be added to or subtracted from the datum volume. The pressure and volume of compressed gas are thus accurately determined.

A gauge of these dimensions used in this manner for pure nitrogen gives consistent results over the range 1×10^{-4} to 2×10^{-1} mm. of Hg with an error not exceeding 4×10^{-5} mm. Qualitative indications of much smaller pressures can be obtained. With air the results are less consistent.

In addition to the gauge the apparatus comprised a 500 c.c. flask as further reservoir space for the gas, and a detachable silica container for the charcoal. The latter was furnished with a mercury-sealed vacuum tap and a side tube ground to fit into a ground cup fused to the apparatus, to which it was sealed with vacuum wax after the "furnacing" of the charcoal had been carried out. All other connexions were of fused glass. The whole apparatus could be put into communication with high vacuum pumps.

The procedure was essentially the same for both the air and nitrogen experiments. The charcoal vessel being attached, the whole apparatus is evacuated to $<1\times10^{-5}$ mm. Hg, and maintained at this for several hours. No appreciable pressure must accumulate during 30 minutes of "rest." The charcoal being shut off, the gas is admitted to the main apparatus and its pressure adjusted to or near the required value *. Time is allowed for equalization of the pressure throughout the apparatus, after which this initial pressure is read. This is corrected for the expansion which takes place into the free space over the charcoal when the latter is opened up by means of the vacuum tap to the rest of the apparatus. After a sufficient time of contact between gas and charcoal the final pressure is read, and this is the equilibrium pressure for a quantity of gas adsorbed which is simply related to the pressure change. Thus we obtain data for a point on the curve. Different points are obtained from different initial pressures. The quantity of gas adsorbed for any final pressure is obtained, in the case of air, by adding together all preceding pressure changes. Large errors were found to be introduced in this way †, and because of this and of the fact that the McLeod gauge does not give consistent results with air, the air results are not regarded as much more than semi-quantitative. In the more exact measurements on nitrogen the charcoal was evacuated (at 25° C. with the pumps) between *each* two points, so that only two pressure measurements were involved in the calculation of any quantity value. For purposes of comparison quantities of gas are referred to one gram of charcoal in all cases. The charcoal bulb was maintained at 25° C. ± 0·05°. The rest of the apparatus was at 17° C. ± 2°.

The Results with Air.

Three different charcoals, each evacuated for four hours at 800° C., were employed. The cooled charcoals were re-evacuated at 25° C. until they ceased to evolve a measurable pressure of gas in a period of 18–24 hours. The air used in the experiments was drawn from the atmosphere through soda-lime, calcium chloride, and finally phosphorus pentoxide, into the apparatus. The results obtained are given in the following Tables, in which P represents the initial pressure, P_f the final equilibrium pressure, and P_c the fall in pressure due to adsorption. A period of 30 minutes was allowed for equilibrium for all points.

---

* By operating a tap leading to the pumps.

† Evident from the trial experiments with N_2—especially on desorbing—due only to accumulated errors in pressure readings.

Results with Air at 25° C. (pressures in mm. of Hg).

TABLE I.

Birchwood Charcoal (1·765 grams).

P_i.	P_f.	P_c.	$\Sigma P_c \div 1{\cdot}765$.
$7{\cdot}7\times10^{-5}$	$4{\cdot}9\times10^{-5}$	$2\ 8\times10^{-5}$	$2{\cdot}8\times10^{-5}$
22·8 ,,	15·0 ,,	7·8 ,,	10·6 ,,
24·0 ,,	19·0 ,,	5·0 ,,	15·6
31·3 ,,	23·0 ,,	8·3 ,,	23·9 ,,
37·5 ,,	25·2 ,,	12·3 ,,	36·2 ,,

TABLE II.

HCl extracted Birchwood Charcoal (1·783 grams).

P_i.	P_f.	P_c.	$\Sigma P_c \div 1{\cdot}783$.
$3{\cdot}3\times10^{-5}$	$2{\cdot}3\times10^{-5}$	$1{\cdot}0\times10^{-5}$	$1{\cdot}0\times10^{-5}$
25·6 ,,	2·7 ? ,,	22·9 ,,	23·9 ,,
193·0 ,,	147·0 ,,	46·0 ,,	69·9 ,,
203·0 ,,	152·0 ,,	50·5 ,,	120·4 ,,

TABLE III.

Coconut Charcoal (4·077 grams).

P_i.	P_f.	P_c.	$\Sigma P_c \div 4{\cdot}077$.
$5{\cdot}6\times10^{-5}$	$3{\cdot}7\times10^{-5}$	$1{\cdot}9\times10^{-5}$	$1{\cdot}9\times10^{-5}$
38·5 ,,	17·8 ,,	20·7 ,,	22·6 ,,
44·8 ,,	31·0 ,,	13·8 ,,	36·4 ,,
41·5 ,,	30·2 ,,	11·3 ,,	47·7 ,,
52·5 ,,	37·5 ,,	15·0 ,,	62·7 ,,
49·4 ,,	35·2 ,,	14·2 ,,	76·9 ,,
205·0 ,,	143 0 ,,	62·0 ,,	138·9 ,,

It will be noticed throughout how near P_f is to the partial pressure of nitrogen in the initial charge, *i. e.* to $\frac{4}{5}$ of the initial pressure. Very little nitrogen appears to be adsorbed. In Table III. the third and fourth final pressures are practically identical, although a further considerable amount of gas has been adsorbed in the case of point four. This is true also of points five and six. In these cases the whole of the pressure fall is due to adsorption of oxygen. If the final pressures are due practically entirely to nitrogen the non-adsorption of nitrogen in the case of points four and six would be expected, for here the initial pressures of nitrogen barely exceed the final pressures (due to nitrogen) of points preceding. The oxygen equilibrium pressures, on the other hand, are considered to be very low, in view of Lowry and Hulett's results [*], where it is shown that such quantities of oxygen as are here adsorbed are not recoverable at ordinary temperatures, *i. e.* the equilibrium pressure is very low. That the total amount of nitrogen adsorbed was small and the oxygen not recoverable was fully confirmed by opening up the charcoal to the evacuated apparatus at the end of each run. In no case was more than a trace of gas evolved.

The importance, from the present point of view, of determinations with pure nitrogen is apparent from these results with air.

The Resvlts with Nitrogen.

The preceding results indicate that the amounts of nitrogen adsorbed at these low pressures are exceedingly small, and consequently that any direct measurements must be carried out on very pure nitrogen. A trial run on atmospheric nitrogen from a cylinder showed that the impurities present masked the results entirely, causing irregularity and very marked hysteresis. Only with pure chemical nitrogen could consistent results be obtained. This nitrogen was obtained by the hypochlorite-urea reaction and purified by passage in order through dilute sulphuric acid, over heated copper gauze, soda-lime and phosphorus pentoxide. It was stored over the latter reagent.

The nitrogen pressures were read in duplicate and mean values used.

All points, with the exception of three referred to later, were determined from zero, *i. e.* on the charcoal freshly evacuated at 25° C.

The volume of the apparatus, determined by expanding nitrogen from the gauge, was 787 c.c. The free space over the charcoal in the container was estimated at 11·35 c.c. The pressure change due to expansion of the gas into the free space is thus of the same order as that due to adsorption, and has accordingly been allowed for throughout.

---

[*] Lowry and Hulett, J. A. C. S. xlii. p. 1408 (1920).

Equilibrium between gas and charcoal was found to be rapidly attained, the same results being obtained with 10 minutes, 30 minutes, or 17 hours of contact. In one case the charcoal was evacuated rapidly from 1×10^{-2} mm. (nitrogen) to zero and then left for 48 hours. No measurable pressure was found to have developed at the end of this period.

Through pressure of other work the nitrogen determinations had to be confined to one charcoal, viz. steam-activated coconut charcoal evacuated for four hours at 800° C. (re-evacuated cold as foregoing samples). Weight of charcoal =4·087 grams.

The results follow in Table IV.

Adsorption of Nitrogen at 25° C.

TABLE IV.

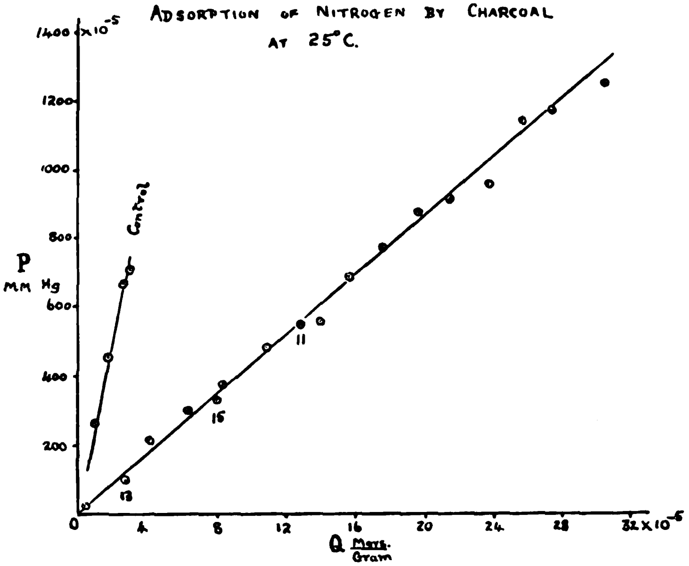
No.	Pressures in mm. of Hg.			Mgrs. N_2 adsorbed.	Mgrs. per gram charcoal.
	P_i.	P_f.	P_c.		
1 ...	$225·6 \times 10^{-5}$	$211·7 \times 10^{-5}$	$13·9 \times 10^{-5}$	$16·9 \times 10^{-5}$	$4·1 \times 10^{-5}$
2 ...	384·7 ,,	356·6 ,,	28·1 ,,	34·3 ,,	8·3 ,,
3 ...	516·4 ,,	479·7 ,,	36·7 ,,	44·7 ,,	10·9 ,,
4 ...	735·4 ,,	682·5 ,,	52·9 ,,	64·5 ,,	15·7 ,,
5 ...	988·7 ,,	915·6 ,,	73·1 ,,	89·1 ,,	21·6 ,,
6 ...	1037·5 ,,	957·0 ,,	80·5 ,,	98·2 ,,	23·9 ,,
7 ...	1232·0 ,,	1145·0 ,,	87·0 ,,	106·1 ,,	25·8 ,,
8 ...	598·3 ,,	551·1 ,,	47·2 ,,	57·5 ,,	14·0 ,,
9 ...	942·3 ,,	876·0 ,,	66·3 ,,	80·8 ,,	19·7 ,,
10 ...	314·4 ,,	293·2 ,,	21·2 ,,	25·8 ,,	6·3 ,,
11 ...	568·2 ,,	546·3 ,,	+21·9 ,,	52·5 ,,	12·8 ,,
12 ...	835·1 ,,	775·7 ,,	59·4 ,,	72·4 ,,	17·6 ,,
13 ...	44·0 ,,	93·7 ,,	−49·7 ,,	11·8 ,,	2·8 ,,
14 ...	1267·0 ,,	1174·0 ,,	93·0 ,,	113·4 ,,	27·6 ,,
15 ...	263·4 ,,	328·9 ,,	−65·5 ,,	33·5 ,,	8·1 ,,
16 ...	1354·0 ,,	1251·0 ,,	103·0 ,,	125·6 ,,	30·6 ,,
17 ...	24·0 ,,	22·7 ,,	1·3 ,,	1·6 ,,	0·4 ,,

Fig. 2 shows the plot of the equilibrium pressures P_f against the quantities in $\frac{\text{mgrs.}}{\text{gram.}}$

The only points that were not determined on the freshly evacuated charcoal were points 11, 13, and 15 (*vide* Table IV.).

Point 11 was obtained in two stages, the first stage being point 10. The pressure fall of point 11 has been added to that of point 10 before calculating the quantity of gas adsorbed. It will be seen that point 11 lies well on the curve. This adsorption point, obtained in more than one stage, has been included to show that there is no fundamental difference in the final values whether they are arrived at in one stage or more. However, if many quantities are added in this way, a gradual accumulation of errors results, particularly evident on attempting to reverse the adsorption process *.

Fig. 2.



Points 13 and 15 are desorption points carried out from points 12 and 14 respectively. Here the initial pressures in the apparatus were less than the equilibrium pressures over the charcoal, and consequently a rise in pressure, corresponding to a loss of gas from the charcoal, took place. These pressure changes have been subtracted from those of the preceding points, before calculating the quantity of gas remaining in the charcoal.

The weights of gas adsorbed were calculated from the pressure changes and the volume of the apparatus (787 c.c.) using the gas laws. Mean T = 290° abs.

The time allowed for attainment of equilibrium in this final series of measurements was 10 minutes, which, as

---

* Observed in the preliminary experiments not described here.

previously stated, was found to lead to the same results as much longer times of contact between gas and charcoal.

The points were actually determined in the order shown in Table IV.

In view of the minuteness of the quantities of nitrogen adsorbed, it was thought desirable to investigate any effect due to the interior surface of the charcoal container (silica). This was done by carrying out a few precisely similar measurements with the same container, but with the charcoal removed and replaced by the same volume of mercury. No effects beyond those due to expansion (from the apparatus reservoir into the evacuated container), as the following table shows, were found. As before stated, these were allowed for in the measurements on nitrogen and charcoal.

TABLE V.

Control experiment without Charcoal.

P_i.	P_f.	P_e obs.	P_c calc.
$266{\cdot}8\times10^{-5}$	$263{\cdot}6\times10^{-5}$	$3{\cdot}2\times10^{-5}$	$3{\cdot}7\times10^{-5}$
461·2 „	455·6 „	5·6 „	6·4 „
711·6 „	701·6 „	10·0 „	10·0 „
680·0 „	671·0 „	9·0 „	9·5 „

Pressures in mm. of Hg.

To show the behaviour of the McLeod gauge, these observed pressure changes due to expansion were divided by the weight of charcoal, converted to mgrs. of N_2, and plotted against the final pressures in fig. 2 alongside the adsorption curve.

DISCUSSION.

These two curves represent exactly comparable results obtained with and without charcoal. What is important to notice is that both pass through the origin and the adsorption curve is, in addition, reversible. Apparently Rowe* did not test the reversibility of his curves. In the author's view some such test of the reliability of the results is essential before they can be accepted and formulæ applied. The results obtained in the preliminary work where less care was taken in using the gauge, in purifying the nitrogen, and where the charcoal was not evacuated between each two points on the curve, were not reproducible nor was any curve reversible, and, if the present results are taken as correct, large relative errors were committed. The acceptance or rejection of a particular formula on such results would have been quite unwarranted.

---

* Phil. Mag. i. p. 109 (1926).

It will be seen that the nitrogen adsorption curve shows the quantity of nitrogen adsorbed to be a linear function of the pressure, i. e. $q = Kp$. These results show K to have the value 0·023 when q is in $\frac{\text{mgrs.}}{\text{gram}}$ and p in mm. of mercury. This is in agreement with the results of Claude*, who also found at −183° C. a linear relation between quantity of nitrogen adsorbed and the pressure in the low pressure region. The Freundlich adsorption formula is $q = Kp^{1/n}$. If this formula applies to the present results, then $n = 1$ for nitrogen in this pressure region.

The results show that equilibrium is rapidly attained and is set up from either direction with completeness in a time not greater than that required for equalization of pressure throughout the apparatus employed. They show also, incidentally, that nitrogen is completely and readily recoverable from charcoal at ordinary temperatures by evacuation. For, if this were not so, point one, obtained on the nitrogen-free charcoal, would not lie on the same curve as the other points, nor would the curve be regular if a variable amount of nitrogen were left in the charcoal after evacuating for each new point.

SUMMARY.

1. The isotherm for nitrogen and charcoal at 25° C. has been determined between the pressure limits 2×10^{-4} and $1{\cdot}3 \times 10^{-2}$ mm. of Hg.
2. At this temperature and in this pressure region the quantity of nitrogen adsorbed is a linear function of the pressure.
3. The isotherm is reversible and equilibrium is rapidly attained.

The author wishes in conclusion to express his best thanks to Professor A. J. Allmand for helpful criticism throughout the work.

University of London,
King's College,
May 1926.

---

* *Comptes Rendus*, clviii. p. 861 (1914).

CXV. *On Sir J. J. Thomson's Model of a Light-Quantum.*

By Prof. N. P. KASTERIN, *Research Institute of the 1 Moscow University* *.

IT is commonly accepted that the quantum theory is almost incompatible with Maxwell's equations ("Clerk Maxwell's Electromagnetic Theory," by H. A. Lorentz, the Rede Lecture, 1923, p. 34); however, Sir J. J. Thomson † constructed a most valuable model of a light-quantum which, as will be shown, is formally consistent with the system of Maxwell's equations.

By the way of examining the simplest case of a light-quantum, we shall explain the difference of the Faraday-Maxwell-J. J. Thomson's electrodynamics from the usual Maxwell-Hertz-Lorentz's interpretation of an electromagnetic field, the form of the differential equations for the free æther being the same in both theories.

The light-quantum in the model of Sir J. J. Thomson consists in a ring-shaped Faraday tube moving with the speed of light at right angles to its own plane. The ring is preceded and followed by ordinary waves of feeble intensity; their wave-length is equal to the circumference of the ring. The energy contained in such a ring will be of the form $h\nu$ (Planck's law) if we admit, with Sir J. J. Thomson, that the cross-section of the tube is proportional to the square of the radius of the ring.

These two fundamental laws, as will be shown, are formally in accordance with the system of Maxwell's equations under the condition that we accept Sir J. J. Thomson's interpretation of an electromagnetic field.

Let $\mathbf{E}_a$ (fig. 1) be a closed ring-shaped Faraday tube referred to fixed axes. Let us suppose that at $t=0$ the plane of the ring coincides with the plane ZOY, and that $\mathbf{u}_x$ is the velocity of the ring. The Maxwell's equations for the free æther are of the form

$$\operatorname{div} \mathbf{E} = 0, \quad \ldots \quad (1)$$

$$\operatorname{curl} \mathbf{M} = \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t}, \quad \ldots \quad (2)$$

$$\operatorname{div} \mathbf{M} = 0, \quad \ldots \quad (3)$$

$$\operatorname{curl} \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{M}}{\partial t}, \quad \ldots \quad (4)$$

---

* Communicated by the Author.

† "A Suggestion as to the Structure of Light," Phil. Mag. [6] xlviii. p. 737 (1924); "The Structure of Light," Phil. Mag. l. p. 1182 (1925).

where c is the velocity of light, $\mathbf{E}$ the electric and $\mathbf{M}$ the magnetic intensity. In the case of stationary motion the operation $\frac{1}{c}\frac{\partial}{\partial t}$ will be replaced by $-\beta_x\frac{\partial}{\partial x}$ if $\beta_x=\frac{\mathbf{u}_x}{c}$, and the equations (2) and (4) will be transformed into

$$\operatorname{curl}\overline{\mathbf{M}}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

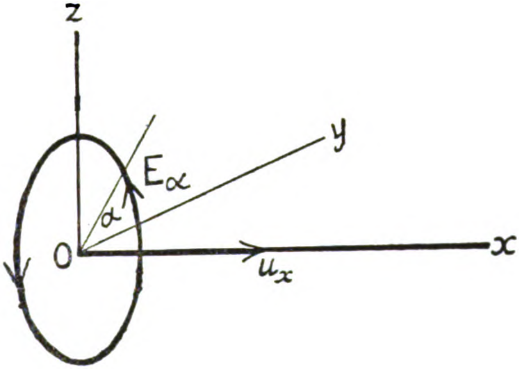
and $$\operatorname{curl}\overline{\mathbf{E}}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4')$$

where $\overline{\mathbf{M}}$ has for components

$$\mathbf{M}_x,\ \mathbf{M}_y+\beta_x\mathbf{E}_z,\ \mathbf{M}_z-\beta_x\mathbf{E}_y$$

and $$\overline{\mathbf{E}} \ldots\ldots \mathbf{E}_x,\ \mathbf{E}_y-\beta_x\mathbf{M}_z,\ \mathbf{E}_z+\beta_x\mathbf{M}_y.$$

Fig. 1.

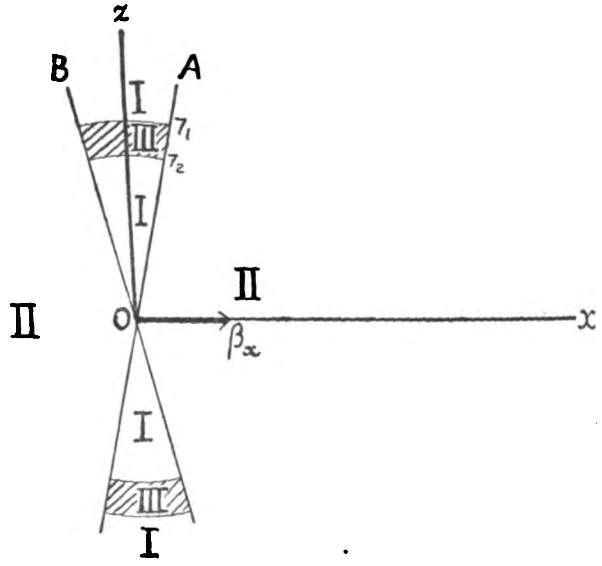


The simplest solutions of the equations (2′) and (4′) are the following: $\overline{\mathbf{M}}=0$ and $\overline{\mathbf{E}}=0$ for the whole space. Now $\overline{\mathbf{M}}=0$ gives $\mathbf{M}_x=0$, $\mathbf{M}_y=-\beta_x\mathbf{E}_z$, and $\mathbf{M}_z=\beta_x\mathbf{E}_y$. Since $\overline{\mathbf{E}}=0$, we have $\mathbf{E}_x=0$, $\mathbf{E}_y(1-\beta_x^2)=0$, and $\mathrm{E}_z(1-\beta_x^2)=0$. These equations can be satisfied by *two* different suppositions:

$$\mathbf{E}_x=0,\ \mathbf{E}_y=0,\ \mathbf{E}_z=0\ ;\ \text{or}\ \mathbf{E}_x=0,\ \mathbf{E}_y\neq0,\ \mathbf{E}_z\neq0,\ 1-\beta_x^2=0.$$

Let us divide the whole space round the point O into *three* parts:—Part I, annular space between two cones (fig. 2), obtained by rotation of OA and OB round the x-axis, having a common vertex at O, the angle AOB being infinitesimal. Part II, the inside of the above-mentioned cones. Part III is taken out of I by the spheres of r_1 and r_2, with the centre at O. For parts I and II we take the first solution of the equations (2′) and (4′), *i. e.* $\mathbf{E}_x=0$, $\mathbf{E}_y=0$, $\mathbf{E}_z=0$; hence $\mathbf{M}_x=0$, $\mathbf{M}_y=0$, $\mathbf{M}_z=0$. For the region III we take the second solution: $\mathbf{E}_x=0$, $\mathbf{E}_y=-\mathbf{E}_\alpha \sin\alpha$, $\mathbf{E}_z=\mathbf{E}_\alpha\cos\alpha$, $\mathbf{E}_\alpha\neq 0$, $\beta_x=+1$; hence $\mathbf{M}_x=0$, $\mathbf{M}_y=-\mathbf{E}_\alpha\cos\alpha$, $\mathbf{M}_z=-\mathbf{E}_\alpha\sin\alpha$. Thus we obtain an electric field *only* in the region III. This field is moving with the velocity of light (first law of the light-quantum theory). If we transform the equation $\operatorname{div}\mathbf{E}=0$, using polar coordinates r, ϕ, α, we obtain $\frac{\partial \mathbf{E}_\alpha}{\partial\alpha}=0$. Thus $\mathbf{E}_\alpha$ is a function of r only; the cross-section of the Faraday tube is constant.

Fig. 2.



The equation $\operatorname{div}\mathbf{M}=0$, which is also to be solved for the region III, after transformation takes the form

$$\frac{\partial}{\partial r}(r^2\mathbf{M}_r)=0 \quad \ldots\ldots \quad (5)$$

or

$$\frac{\partial}{\partial r}(r^2\mathbf{E}_\alpha)=0. \quad \ldots\ldots \quad (5')$$

Here, namely in this equation (5), lies the divergence between the Maxwell-Hertz-Lorentz electrodynamics and the theory of Faraday-Maxwell-J. J. Thomson. From the standpoint of the first theory the equation (5) is valid in the whole space occupied by the free æther, and consequently will be valid in regions I and III and at their boundaries. So that if we admit $\mathbf{E}_\alpha=0$ and $\mathbf{M}_r=0$ for the region I, the constant in the solution $\mathbf{E}_\alpha=\frac{\text{const.}}{r^2}$ of the equation (5′) for the region III must also vanish. So, according to the first theory, there can be no electromagnetic field in the region III, since there is no field in the regions I and II. We cannot admit the existence of a field in the region I, as it must have the form $\mathbf{E}_\alpha=\frac{\text{const.}}{r^2}$, which gives for the point O, $\mathbf{E}_\alpha=\infty$.

From the point of view of Sir J. J. Thomson's theory the structure of the field is *discontinuous*. The field consists in a system of Faraday tubes moving relatively to one another; the intensity of the magnetic field is determined by the intensity of the electric field and by the normal velocity β_n of the tube, from the equation $\mathbf{M}=\beta_n\mathbf{E}$. It follows (1) that the equation (2′) is satisfied identically; (2) that the intensity $\mathbf{M}$ has a definite value different from zero only where the Faraday tubes are in motion. The equation (3), $\operatorname{div}\mathbf{M}=0$, exists only where the Faraday tubes are in motion; in the rest of the free æther $\mathbf{M}$ does not exist. If we admit the theory of J. J. Thomson, the equation $\operatorname{div}\mathbf{M}=0$ must be satisfied in our case *only* in the region III up to its boundaries of II. At the boundary I–III we may have a discontinuity of $\mathbf{M}_r$ and consequently of $\mathbf{E}_\alpha$. Hence for the region III we may satisfy (5′) by the supposition $\mathbf{E}_\alpha r^2=$ finite constant.

Calculating the energy of the ring, we obtain

$$\frac{1}{8\pi}(\mathbf{E}^2+\mathbf{M}^2)\times\text{volume of the ring}=2\,.\,\tfrac{1}{2}\epsilon\,.\,\mathbf{E}_\alpha\,.\,2\pi r=\frac{2\pi^2\epsilon^2}{c\phi_0}\,.\,\nu,$$

where ϵ is the charge of the electron, $\frac{\nu}{c}=\frac{1}{2\pi r}$, and $\epsilon/2\phi_0$ the constant of integration. Thus we obtain the second law of the light-quantum theory (Law of Planck).

From the preceding considerations we may conclude that the Maxwell's equations actually lead to the solution given by Sir J. J. Thomson.

It seems to me also that the difference between the

Maxwell-Hertz-Lorentz electromagnetic theory and the theory of Faraday-Maxwell-J. J. Thomson might be *analytically* formulated as follows :—(1) For the free æther the differential equations are the same in both theories, being the Maxwell's system :

$$\operatorname{div} \mathbf{E} = 0, \quad \ldots \ldots \quad (1)$$

$$\operatorname{curl} \mathbf{M} = \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t}, \quad \ldots \ldots \quad (2)$$

$$\operatorname{div} \mathbf{M} = 0, \quad \ldots \ldots \quad (3)$$

and

$$\operatorname{curl} \mathbf{E} = \frac{1}{c} \frac{\partial \mathbf{M}}{\partial t}. \quad \ldots \ldots \quad (4)$$

(2) The first theory postulated that all these equations are valid in the *whole* space filled by the free æther ; in the second theory the equation (3) occurs *only* where we have a moving electric field. Formulating this difference *geometrically*, we may say that the electric lines of force in the free æther are everywhere continuous, while the magnetic may be *discontinuous* : they must end on the boundaries dividing the moving Faraday tubes from those at rest. This circumstance gives the possibility of introducing *discontinuities* in electromagnetic field, and enormously increases the variability of the special instances, which satisfy the Maxwell systems of equations. The Maxwell equations, as it has been shown above, admit such forms of electromagnetic fields as have the same properties as the light-quanta.

It seems to me that this interpretation enables us to construct, on the basis of Maxwell's equations, investigating them for the case $\beta_n^2=1$, a *rational* quantum theory.

Research Institute of the
1 Moscow University,
1 April, 1926.

CXVI. *The Resistance of High-Frequency Circuits.* *By* R. R. Ramsey, *Ph.D., Professor of Physics, Indiana University* *.

THE resistance of a high-frequency circuit is apparently easy to determine. However, the separation of the resistance of the coil from that of the condenser is a difficult matter.

It has been customary to consider the resistance of the condenser small enough to be neglected, so that the entire resistance of the circuit is ascribed to the coil.

The first attempt to measure the resistance of a condenser at high frequency was made a little more than a year ago by Weyl and Harris (Institute of Radio Engineers, Proc. vol. xiii. p. 109, Feb., 1925). In this work the resistance of a rectangular coil approximately eighteen feet by twenty-five feet was calculated, assuming the resistance of the rectangle at the given frequency to be the same as the high frequency resistance of a straight wire of the same diameter, whose length was the same as the perimeter of the coil. The resistance obtained in this manner varied with the capacity of the condenser from one ohm at ·0005 microfarad to about twenty ohms at ·00005 microfarad.

Callis (Phil. Mag. vol. i. p. 428, Feb. 1926) has made measurements in which he used coils made of No. 36 and No. 40 copper wire. The method used was to measure the resistance of a circuit with a coil and condenser at a given setting using the resistance variation method, then to measure the resistance of the circuit again after the first coil had been replaced by one made exactly like the first. Then the two were connected in series opposition and their position adjusted, so the combined inductance of the two was the same as the inductance of a single coil, and the combined resistance was measured again. From these results the resistance of the condenser could be eliminated and the resistance of the coils determined. Since the results gave the resistance of the coils to be the same as the D.C. resistance, it was assumed that the resistance of small wire wound in a coil was the same as the resistance of the wire when straight, which was very close to its D.C. resistance at a frequency of one million. From these same equations the resistance of the condenser was determined. It was found that the resistance of a

---

* Communicated by the Author.

41 plate variable condenser of the "low loss" type varied from 1·5 ohms at ·001 microfarad capacity to 15 ohms at ·00001 microfarad.

Maibauser and Taylor (Phys. Rev. vol. xxvii. p. 251, 1926), in the abstract of a paper presented before the American Physical Society, state that they have found the resistance of a variable condenser to be so large that the usual assumption that the resistance of the condenser is small enough to be neglected was not justified. However, the abstract does not give the values found.

All these results are much larger than the usual assumption,—so much larger that they may be said to be revolutionary. These experimenters find that the resistance of a good variable condenser varies from near one ohm at full capacity to fifteen or more at small capacity. The resistance varies as the reciprocal of the capacity, and the resistance may be said to be proportional to the reciprocal of the capacity as a very close approximation to the law.

The writer has tried to devise some circuit so as to verify these results. He tried measuring condensers in series and in multiple but could not get a check on the results. If one stops to calculate the resistance of condensers in series or in multiple, assuming that the resistance is proportional to the reciprocal of the capacity, one will find that the resistance of two condensers is equal to the resistance of one condenser. Thus when one condenser was replaced by two in parallel or in series, it was found that the resistance of the two was the same as that of one condenser. If the resistance of a condenser is negligibly small or zero, this is true also.

In order to get a check it was necessary to resort to heat measurements. The condenser or coil was placed in one bulb of a differential air thermometer while a known D.C. resistance was placed in the second bulb. The thermometer was made of two pyrex glass beakers inverted and sealed to glass plates. Through each glass plate three holes were drilled. In two of these holes electrical connexions were sealed, and in the third a glass tube was sealed. By connecting the glass tubes to a U-tube which contained a small amount of water, the relative pressure of the air in the beakers could be determined. Two T-tubes were placed above the U-tube, one under each beaker. By opening these T-tubes the pressure of the air in the beaker could be made equal to the pressure of the atmosphere.

The beakers were sealed to the glass plates with beeswax. At times there was some difficulty in getting the connexion air-tight. This was tested by noting whether the pressure would become equal after a run. If there was evidence that one of the beakers leaked the result was discarded.

The coil or condenser under investigation was placed in one of the beakers and electrical connexions were made with solder. In the second beaker a known D.C. resistance was placed and soldered to the electrical connexions. It was found that when a coil was under investigation the best D.C. resistance to use was a coil which was an exact duplicate of the first coil. When the resistance of a condenser was being measured a short piece of "cromel" resistance wire, 3·4 ohms, was connected to the terminals in the D.C. beaker.

When making a measurement the procedure was as follows:—The coil or condenser was placed in the beaker and connected in a high-frequency circuit which was inductively connected to an oscillating circuit driven by a five-watt tube. The high-frequency circuit was adjusted to the proper current value. The approximate value of the D.C. current was found and then the apparatus was left for some time to cool down to the temperature of the room, the two side T tubes being open. In an hour or more the run proper was made. The side T-tubes were closed and the high-frequency generator was started. The D.C. current was turned on and adjusted so as to keep the pressure equal, as indicated by the water in the U-tube. After some minutes when final equilibrium was obtained the two ammeters were read. The high-frequency ammeter was a Weston 1·5 ampere thermo-ammeter which was correct for D.C. current and guaranteed by the maker to be accurate for 1500 kilocycle current. For small values of radio-frequency current a General Radio 250 milliampere hot wire milliammeter was used. To measure D.C. current a Weston ammeter was placed in the circuit.

When thermal equilibrium is obtained the heat produced in one beaker is equal to the heat produced in the second beaker, assuming the thermal constants of the two beakers to be the same. Then $I^2R=i^2r$, where I and R refer to the current and resistance in the high-frequency circuit and i and r refer to the current and resistance in the D.C. circuit. Then we have the resistance of the radio-frequency circuit $R=(i^2r)/I^2$. Any dielectric losses, eddy current losses, or resistance losses will appear as heat. R, the resistance of the circuit, is the series resistance in the circuit which will produce the same heat as all these effects.

The accuracy of heat measurements is not as great as the accuracy of ordinary resistance measurements, and the accuracy of these measurements is not as great as might be desired, but they are sufficiently accurate to indicate the approximate values and to settle the point in question.

First, coils were measured, and it was found that the resistance of a coil is less than the resistance of the circuit obtained by the resistance variation method. This result indicates that the condenser must have a resistance which cannot be neglected. A condenser was then placed in the beaker and the resistance was found to be very small—about 0·1 ohm—the capacity of the condenser being ·00008 microfarad. This indicates that the heat generated in the circuit is less than the total energy of the circuit.

Table I. gives the data taken using five different coils. A.C. resistance is the resistance of the coil measured by the resistance variation method, assuming the resistance of the condenser to be small. Resistance (Heat) is the resistance obtained by means of the calorimeter.

TABLE I.

Resistance of Coils at 1000 *kilocycles.*

Capacity of condenser in microfarads.	D.C. resistance.	A.C. resistance.	Resistance (Heat).	Inductance in microhenries.	Remarks.
Coils of No. 20 copper wire, 30 turns each.					
·00008	0·35	10·7	8·2	316	Two coils in series.
·00028	0·35	8·3	7·3	91	Two coils series opposition.
·00028	0·175	4·3	3·7	91	Single coil.
Coil of No. 30 copper wire, 20 turns.					
·00020	9·6	19·4	11·5	127	Single coil.
Coil of No. 40 copper wire, 14 turns.					
·00054	16·6	21·1	17·2	47	Single coil.
Coil of No. 40 copper wire, 30 turns.					
·00009	34·3	52·5	36·6	282	Single coil.

Each result given in the above table is the average of a number of separate determinations.

It will be noticed that in every case the resistance as measured by the heat method is less than that measured by the resistance-variation method. The high-frequency resistance of the coil was balanced against the D.C. resistance of a similar coil. As a check the connexions were interchanged so as to test the equality of the thermal constants of the two bulbs. It was found that within the accuracy of the method there was no difference. Instead of a duplicate coil in some cases, the coil was checked against a short piece of resistance wire. These results agreed with the results obtained by using duplicate coils. Since the results obtained by the two methods check, it shows that the resistance of the condenser as given in the following table can be relied upon, as it was necessary to use unsymmetrical circuits when measuring the resistance of the condenser. To make the two circuits and bulbs as symmetrical as possible, a dummy condenser was placed in the D.C. side with the resistance wire in order to make the thermal capacity of the contents of the two bulbs equal.

In Table II., given below, the average of a number of readings is given.

TABLE II.

Resistance of a 11-Plate Condenser set at ·00008 m.f. (about one-third maximum).

	300 metres.	80 metres.	40 metres.	27 metres.
Highest	·15 ohm.			
Lowest	·05 ,,			
Mean	·098 ,,	·06	·04	·06

The results for 80, 40 and 27 metres are too low, since the ammeter in all probability reads too high. In the work at 300 metres it was necessary to keep the current at or below ·8 ampere, since the potential became so high that an arc started between the plates of the condenser when the current was ·9 ampere.

After these results were taken the condenser was compared with three others made by different firms, and it was found that there was no appreciable difference between this condenser and the average condenser.

These results show that the resistance of a good radio condenser is not excessive and that the results of Weyl and Harris, and Callis are entirely too large. Their results must be explained in some other manner. The probable explanation is as follows:—The calorimeter method measures the energy that remains in the pyrex glass beaker. Any energy radiated through the glass will not cause heat. Therefore, there must be an appreciable amount of energy radiated from an ordinary circuit. In other words, there is a certain amount of resistance in the circuit which cannot be ascribed to either the condenser or to the coil.

Bloomington, Indiana, U.S.A.
April 6, 1926.

CXVII. *The Radioactivity of Potassium and its Geological Significance.* By Arthur Holmes, *D.Sc., A.R.C.S., F.G.S., University of Durham, and* Robert W. Lawson, *D.Sc., F.Inst.P., University of Sheffield* *.

CONTENTS.

I. The Problem of the Pre-Cambrian Granites.
II. The Radioactive Constants of Rubidium and Potassium.
III. The Emission of Energy by Rubidium and Potassium.
IV. Possible Effects other than Thermal.
V. The Average Thickness of the Continents.
VI. The Nature of the Substratum.
VII. Geological Time and Latent Heat.
VIII. Conclusions.

I. *The Problem of the Pre-Cambrian Granites.*

It is a well-known fact of geological history that the greatest and most widespread intrusions of granitic rocks were those which invaded the continental crust during the earlier Pre-Cambrian eras. According to Daly, more than nine-tenths of the world's granites are of Pre-Cambrian age †. In later ages the more voluminous intrusions of granite and granodiorite have been restricted to belts characterized by intense mountain-building movements, such, for example, as those known as the Caledonian, Hercynian, and Appalachian. The great Pre-Cambrian shields have not been visibly penetrated by granite on an

---

* Communicated by the Authors.

† 'Igneous Rocks and their Origin,' p. 57 (1914).

important scale since the close of the Pre-Cambrian, except in the immediate neighbourhood of the bordering geosynclines and mountain belts. Moreover, the earlier invasions were on a far greater scale than those that followed. The continents began as great granitic regions, and through them surged four or more successive waves of granitic magma at long intervals, gradually becoming less voluminous —or less penetrative—as time went on, until by the end of the Pre-Cambrian eras that particular manifestation of regional magmatic activity came to an end, so far as the levels of the crust which are accessible to observation are concerned.

It is easy at the present day to understand why there should be no evidence of the development of such magmas during the later geological periods, because the radioactivity of the rocks is insufficient to generate the necessary heat for the production, within the continents, of the enormous volumes of magma, which alone could ascend so high that denudation should afterwards be able to disclose the rocks consolidated from them. The condition for the occurrence of such phenomena would be a far greater continental thickness than we can justifiably assume. Incidentally, this consideration explains why, in the later periods, granitic magmas have been generated deep within the cores of mountain ranges, for such situations are precisely those in which, because of compression, the continental rocks have been locally thickened *.

The problem thus arises as to how it was that such regional phenomena occurred, and occurred on a decreasing scale, during the Pre-Cambrian eras. Were the continents far thicker then than now, or was the radioactive generation of heat more potent to provide the necessary supplies? The first assumption would lead to the conception of highland continents which could never have come beneath the waves. Yet we know that the lands were then, as afterwards, subject to marine transgressions and recessions. The second assumption would lead to the conclusion that basaltic lavas should also have been more abundant than in more recent periods. Again we know that they were not, for the eruptions of plateau-basalts in North and South America, the Brito-Arctic region and the Deccan, which occurred between the beginning of the Jurassic and the middle of the Eocene, were on as vast a scale as anything of which we have evidence from the Pre-Cambrian.

---

* A. Holmes, Geol. Mag. lxii. pp. 507 & 533–534 (1925).

The extra source of heat must therefore be looked for either in the former distribution of the radioactive elements, or in the presence in the granitic rocks of some radioactive element not specially characteristic of basaltic rocks. It was the latter consideration that led us to suspect potassium as a possible active thermal agent. The joint investigation, of which this paper is a record, was therefore undertaken. The surprising result has emerged that potassium, on account of its great abundance in the rocks, is an emitter of radiothermal energy of the same order of importance as either uranium or thorium*. Rubidium is clearly negligible from the geological standpoint on account of its extreme rarity, despite the fact that its total activity is greater than that of an equal amount of potassium.

It was thought possible that the radioactivity of potassium might have been greater in early geological time than it is now, and so have led to the extensive intrusions of granite that then took place. It is, however, not yet possible to draw any such conclusion from the available data, nor will it become possible, unless future investigations indicate that the activity is confined to a still undiscovered isotope, which has been appreciably wearing out during geological time. Unfortunately, the detection of an end-product (isotope of calcium) in old potassium minerals is not practicable, owing to the very slow rate of decay of potassium. Meanwhile, the problem of the Pre-Cambrian granites remains unsolved, though it is not improbable that the explanation lies in the formerly more uniform distribution of potassium through the depths of the continents. Later intrusions would inevitably tend to concentrate potassium, as well as uranium and thorium, towards the surface, and so to reduce the temperatures natural to the lower regions of the continents. Thus in the early ages the ascent of heat from the substratum beneath the continents would be more effective in promoting fusion than it is now.

II. *The Radioactive Constants of Rubidium and Potassium.*

Of the alkali metals, only rubidium and potassium show a measurable radioactivity. Whereas potassium emits β-rays of greater penetrating power than rubidium, it is generally recognized that the total activity (ionization corresponding to complete absorption) of rubidium is greater than that of an equal amount of potassium, though the estimates of the total relative activities vary within wide limits (1·4/1—

---

* A. Holmes & R. W. Lawson, 'Nature,' cxvii. p. 620 (1926).

Harkins and Guy, and 7/1—N. R. Campbell)*. The considerations set forth in the preceding section were responsible for our undertaking an examination of the extent to which the elements rubidium and potassium have contributed towards the thermal history of the earth, and for this purpose it was necessary to ascertain the radioactive constants of these two elements as accurately as possible from the evidence hitherto accumulated.

In order to obtain the most reliable values of the radioactive constants for these two elements, we have carefully analysed the data available, with the results recorded below. We shall deal first with the velocity and energy of the β-rays emitted by the two substances, and then with their most probable half-value periods, before applying the results to the materials of the earth's crust.

The β-rays from rubidium are fairly homogeneous, and their mean velocity has been determined † by direct comparison of their deflexion in a magnetic field with that of the rays from RaE. In this way the velocity of the rays was found to be about $0·62\,c$. This result is supported by estimates based on measurements of the coefficient of absorption of the rubidium rays. Thus Hahn and Rothenbach ‡ found that the rays are slightly softer than the β-rays from radium, but distinctly harder than the β-rays from UX_1, whence they estimated the velocity to be about $0·58–0·60c$. We obtain a result in substantial agreement with the above, if we apply Lenard's curves of absorption § of β-rays of different velocity to Hahn and Rothenbach's value ($\mu=347$ cm.$^{-1}$ aluminium) for the coefficient of absorption of the β-rays from rubidium. We shall therefore assume that the velocity of these rays is $0·60\,c$, or that the kinetic energy of a single β-ray is $2·04 \times 10^{-7}$ erg.

The β-rays from potassium do not appear to be quite so homogeneous as those from rubidium, the coefficient of absorption varying for different observers from about 16 cm.$^{-1}$ to 50 cm.$^{-1}$ aluminium ‖. Since, however, the rays are on an average only slightly less penetrating than those from

---

* N. R. Campbell, Proc. Cambr. Phil. Soc. xv. p. 11 (1909). E. Henriot, *C. R.* cxlviii. p. 910 (1909). W. D. Harkins & W. G. Guy, Proc. Nat. Acad. Sc. xi. p. 628 (1925). Full references to the earlier literature are given in the standard works of Rutherford, and of Meyer and Schweidler.

† K. Bergwitz, *Phys. Zeit.* xiv. p. 655 (1913).

‡ O. Hahn & M. Rothenbach, *Phys. Zeit.* xx. p. 194 (1919).

§ 'The Structure of the Atom,' Andrade, Appendix I. p. 296 (G. Bell, 1923).

‖ Campbell, etc., *l. c.*

UX_2 ($\mu = 14{\cdot}4$ cm.$^{-1}$ aluminium, $v =$ ca. $0{\cdot}92\,c$), Hahn (*l. c.*) concludes that the average velocity of the β-rays from potassium cannot differ much from $0{\cdot}90\,c$. If we assume μ to be about 20 cm.$^{-1}$ aluminium, Lenard's curves indicate that the velocity will be about $0{\cdot}85\,c$, and this value probably makes sufficient allowance for the heterogeneous nature of the rays. The corresponding kinetic energy of a β-ray from potassium is, then, $7{\cdot}30 \times 10^{-7}$ erg.

We next require the half-value periods (or disintegration constants) of rubidium and potassium. In the case of rubidium, Hahn and Rothenbach (*l. c.*) have compared the activity of the β-rays emitted by 1 gm. of the element with that of the β-rays from the amount of UX_1 in equilibrium with 1 gm. of uranium. Since these two types of ray are of the same order of hardness, it follows that the ratio of the half-periods of rubidium and uranium will be inversely as their activities (viz. 1/15), so that the resulting half-value period of rubidium is 7×10^{10} years. Strictly speaking, we must take account of the different values of k (no. of ions per cm.) for the rays from the two substances, and of the fact that the Loschmidt number (per gm.) is not the same for the two elements. We find the corrected value of T_{Rb} to be $1{\cdot}4 \times 10^{11}$ years.

By using an extremely delicate apparatus, Hoffmann [*] has compared the activities of rubidium and potassium with that of uranium, and he concludes that his measurements confirm the value of the half-period for rubidium given by Hahn and Rothenbach, though his results point to a slightly smaller value for T_{Rb}. From the point of view of the half-value periods of potassium and rubidium, Hoffmann's measurements are probably the most valuable yet available, for they lend themselves to an approximately absolute interpretation when certain plausible assumptions are made, though he does not appear to have applied them in this way. He used two arrangements: (*a*) Method I, in which the active material was distributed on a concentric cylinder a few cms. away from his spherical ionization chamber; and (*b*) Method II, in which the active material was placed in the bounding surface of his ionization chamber; this latter method, however, was not applicable to uranium, owing to the disturbing action of the α-rays. In both methods the apparatus was filled with CO_2 at 1300 mm. pressure.

From known data on the absorption of β-rays in CO_2, and by assuming the constancy of μ/ρ for the β-rays from a given substance, we have applied corrections to Hoffmann's results to take account of the absorption of the rays in his apparatus and in the active film. Moreover, since the ionization produced by a β-ray per cm. of its path (i. e. k) is approximately known for rays of different velocity, we have been able to calculate that the half-period of rubidium is about 25 times that of uranium ($4{\cdot}4\times10^9$ years), *i. e.* $T_{Rb}=1{\cdot}1\times10^{11}$ years, using the results of Method I. The corresponding calculation using the results of Method II gives T_{Rb}=ca. 8×10^{10} years. There is thus satisfactory agreement between the different estimates of the half-value period of rubidium.

---

[*] G. Hoffmann, *Phys. Zeit.* xxiv. p. 475 (1923); *Zeit. f. Phys.* xxv. p. 177 (1924).

It appears, then, that the half-period of rubidium cannot be far removed from $T_{Rb}=10^{11}$ years ($\lambda=6{\cdot}9\times10^{-12}$ years^{-1}), and we shall make use of these values in our subsequent considerations.

Unfortunately, the data for potassium are not known to the same degree of accuracy as those for rubidium, and further work is desirable with this element. It has already been mentioned that the estimates of the total activity (corresponding to complete absorption) of rubidium relative to that of an equal weight of potassium vary between 7 and 1·4. If we assume that the total ionization produced by a β-ray is proportional to its initial energy, and take account of the difference of the Loschmidt number (per gm.) for these two elements, the above estimates of the total relative activities indicate that the half-value period of potassium is respectively 50 or 11 times that of rubidium. Assuming $T_{Rb}=10^{11}$ years, the corresponding values for potassium are $T_K=5\times10^{12}$ and $1{\cdot}1\times10^{12}$ years respectively. In deciding between these extreme values of the half-period of potassium we can again appeal to Hoffmann's delicate measurements, by applying corrections to his results in the manner indicated above for rubidium. From the results of Method I we find that the half-period of potassium is about 14 times that of rubidium, or 22 times according to Method II. Hoffmann's measurements thus indicate that the half-value period of potassium is $T_K=1{\cdot}4\times10^{12}$ years (Method I), or $2{\cdot}2\times10^{12}$ years (Method II), the former value being probably the more reliable.

We do not believe that the correct value of T_K exceeds about 2×10^{12} years, and consider that the evidence points to $T_K=1{\cdot}5\times10^{12}$ years ($\lambda=4{\cdot}6\times10^{-13}$ year^{-1}) as being the most representative value in the present state of our knowledge. We shall assume these values of T_K and λ in what follows. It should be mentioned that Hahn and

Rothenbach's estimate of the half-period of potassium, based on the relative activities of potassium and rubidium, is from 3 to 7 times that of rubidium, but that they only intended to indicate the general order of magnitude of the result.

In our previous considerations we have assumed that the whole of potassium is radioactive, whereas theoretical considerations render it probable that the activity will be a property of the isotope K_{41}, rather than of K_{39}. The decision of this point must await further experimental investigation. Should the radioactivity be due to K_{41}, our previous estimate of the disintegration constant would require to be increased 20 times, so that we should have $T=7 \cdot 5 \times 10^{10}$ years. Early Archæan rocks (age of the order and greater than 10^9 years)* would then have been heated by the contained potassium slightly more than at present, but as the increase is not more than one per cent., it can be neglected in geothermal problems. Should the activity be due to a hitherto undiscovered isotope, of atomic weight say 40, its increased effect in early geological time might demand consideration.

III. *The Emission of Energy by Rubidium and Potassium.*

We are now in a position to calculate the annual heat production of 1 gram of potassium and rubidium respectively, from which, by making use of the content in average rock of these two elements, we are able to calculate the annual heat production due to potassium and rubidium in each gram of average rock, and similarly for any other kind of rock. The calculations are embodied in the accompanying Table, and for comparison, the annual heat production due to uranium and to thorium (plus disintegration products) per gram of rock are included. The values assumed for the annual heat developed from 1 gram of uranium (0·79 cal. per annum $= 9 \cdot 0 \times 10^{-5}$ cal./hour) and from 1 gram of thorium (0·23 cal. per annum $= 2 \cdot 6 \times 10^{-5}$ cal./hour) have been calculated on the basis of the most recent data, and are in good accord with the values as found experimentally.

It is clear from the Table that the geothermal effect of rubidium is negligible, and the same holds for sodium, which has been found to be practically inactive. On the other hand, the heat developed by the potassium in rocks is comparable with that developed by uranium and by thorium, and must have exerted an important, if not a controlling influence on the igneous history of the earth.

---

* A. Holmes, Phil. Mag. (7) i. p. 1074 (1926).

	Element ...	URANIUM.	THORIUM.	POTASSIUM.	RUBIDIUM.
	Loschmidt Number, N, atoms per gram.	......	......	$15{\cdot}5\times10^{21}$	$7{\cdot}09\times10^{21}$
	Half-value Period, T, in years.	......	......	15×10^{11}	1×10^{11}
	Disintegration Constant, λ, year^{-1}.	......	......	$4{\cdot}6\times10^{-13}$	69×10^{-13}
	Annual Number of Atoms disintegrating per gram, $n=\lambda N$.	......	......	$7{\cdot}1\times10^{9}$	49×10^{9}
	Kinetic Energy, E, ergs per β-ray.	......	......	$7{\cdot}30\times10^{-7}$	$2{\cdot}04\times10^{-7}$
	Energy liberated per gram per year, $nE/(4{\cdot}19\times10^{7})$ cal.	(7900×10^{-4})	(2300×10^{-4})	$1{\cdot}24\times10^{-4}$	$2{\cdot}38\times10^{-4}$
Average Igneous Rock.	Contents in grams per gram of average igneous rock *.	6×10^{-6}	15×10^{-6}	$26{,}000\times10^{-6}$	$m\times10^{-6}$
	Heat generated in cals. per gram of average igneous rock per year.	$4{\cdot}74\times10^{-6}$	$3{\cdot}45\times10^{-6}$	$3{\cdot}22\times10^{-6}$	$2{\cdot}38m\times10^{-10}$
Average Granite.	Contents in gm. per gram of average granite *.	9×10^{-6}	20×10^{-6}	$34{,}000\times10^{-6}$	n.d.
	Heat generated in cals. per gram of average granite per year.	$7{\cdot}1\times10^{-6}$	$4{\cdot}6\times10^{-6}$	$4{\cdot}2\times10^{-6}$	n.d.
Average Plateau-basalt.	Contents in gm. per gram of average plateau-basalt *.	$2{\cdot}2\times10^{-6}$	5×10^{-6}	8000×10^{-6}	n.d.
	Heat generated in cals. per gm. of average plateau-basalt per year.	$1{\cdot}7\times10^{-6}$	$1{\cdot}2\times10^{-6}$	$1{\cdot}0\times10^{-6}$	n.d.

Total Heat in Calories per Year generated in :—

Average Igneous Rock (density$=2{\cdot}75$). $=11{\cdot}4\times10^{-6}$ per gm. $=31{\cdot}4\times10^{-6}$ per c.c.

Average Granite (density$=2{\cdot}65$). $=15{\cdot}9\times10^{-6}$ per gm. $=42{\cdot}2\times10^{-6}$ per c.c.

Average Plateau-Basalt (density$=3$). $=3{\cdot}9\times10^{-6}$ per gm. $=11{\cdot}7\times10^{-6}$ per c.c.
$=13{\cdot}3\times10^{-6}$ per c.c. of eclogite, density$=3{\cdot}4$.

* For the data for radium and thorium, see J. Joly, Phil. Mag. (6) xlviii. p. 819 (1924); and for radium alone, A. Holmes, Geol. Mag. lxii. p. 509 (1925). The figures for potassium are based on thousands of analyses of rocks from all parts of the world.

IV. *Possible Effects other than Thermal.*

It is a well-known fact that the coloration of pleochroic haloes is produced by the action of the α-particles emitted from the central radioactive inclusion, and Lord Rayleigh * has brought forward strong evidence that the colour of zircons, which are always radioactive, is produced in the same way. Since β-rays and γ-rays also produce colorations in minerals when the radiation is of sufficient intensity, it has been suggested that the colour of many minerals may be due to this cause, particularly in view of the widespread occurrence and β-radioactivity of potassium. These latter colorations, however, would be expected to require much longer periods for their development than those due to the much more energetic α-particles. It is, in fact, theoretically possible that the depth of coloration due to the potassium radiation found in a pure potassium mineral free from other colouring agents may serve to give a qualitative idea of the age of the formation in which the mineral occurs, for undoubtedly long periods will be necessary before any colour could appreciably develop from this cause. In practice such effects are likely to be always masked by the presence of other colouring agents.

The more important question arises, however: Is any appreciable fraction of the energy of the radioactive rays used up in producing these colorations? If so, the thermal effect in the mineral will be less than the effect as calculated from the energy of the rays. In a recent Presidential Address before the Geological Society, this question was raised by Dr. J. W. Evans, who stated: "It is certain, however, that the whole of this energy is *not* converted into heat; much of it must be employed in effecting physical, chemical, or atomic changes in the surrounding rock. The substance of the ionized pleochroic haloes in mica is hundreds of thousands of times greater than the radioactive material in the zircon round which they are formed, and they must represent a relatively enormous absorption of energy."

We think, with Lord Rayleigh †, that the evidence decides conclusively against Dr. Evans's view. In all determinations of the heat developed by radium and by it and its disintegration products, the substance has been enclosed in a glass tube of sufficient thickness to absorb the α-rays completely, as well as more than 30 per cent. of the β-rays, and it is well-known that the glass container rapidly becomes coloured by the action of the rays, just as in the case of minerals. We should therefore expect that, if Dr. Evans's view were correct, the heat development as determined experimentally would be distinctly less than the value calculated from a knowledge of the number and energy of the rays involved; but this is far from being the case. Thus for radium alone, *i. e.* without disintegration products, the calculated heat development per gram of the element is 25·47 cals. per hour, whereas the measured value (Hess) is 25·2 cals. per hour, and this experimental value probably requires to be raised by 0·2 or 0·3 cal. per hour owing to incomplete absorption of the γ-rays from radium in the apparatus used [*]. Moreover, the total heat developed by 1 gram of radium together with its short-lived products was found by Rutherford and Robinson to be 135 cals./hour, and by St. Meyer and Hess to be 137 cals./hour, both results probably being somewhat low owing to insufficient allowance for the effect of the γ-rays. Using the latest data, we have calculated the total heat production of radium per gram, including the short-lived products, on the assumption that all the energy is converted into heat, and we obtain the value 137·7 cals./hour. It seems safe to conclude from these results that the energy of the radioactive rays expended in the manner suggested by Dr. Evans does not amount to one per cent. of the total energy, and is probably not more than about one-tenth of this value.

---

* R. J. Strutt, Proc. Roy. Soc. (A), lxxxix. p. 405 (1914).
† Lord Rayleigh, 'The Observatory,' p. 57, Feb. 1926.

V. *The Average Thickness of the Continents.*

The geological consequences of the radioactivity of potassium are clearly of great importance, for the heat generated within the rocks is now found to be considerably greater than the amounts hitherto calculated from uranium and thorium alone.

A maximum estimate of the mean thickness of the average rocks (*sial*) of the continents can be arrived at by equating the amount of heat escaping at the surface with the heat generated within the *sial*. Geothermal gradients are very variable [†], but a reasonable average, sufficiently good for our present purpose, is 35° C. per kilometre. Taking the conductivity as 0·006 C.G.S., the heat lost per annum from a column of 1 sq. cm. cross section amounts to 63 calories, and evidently this could be entirely supplied by 15 km. of average granite (density 2·65), or by 20 km. of average continental rock (density 2·75). On the assumption made, the thickness of the continents should, then, be less than 20 km., for in addition to the heat generated within them, heat must also ascend from the hotter rocks beneath. On no reasonable assumptions whatever is it now possible to admit an average continental thickness of as much as 30 km., though more than 20 km. may still be possible if the radioactivity of the rocks rapidly decreases downwards Like the gradients, the actual thickness must, of course, vary through a wide range, but the average is now definitely limited. Yet, until recently, 30 km. or thereabouts has been the estimate most favoured by seismologists.

---

[*] R. W. Lawson, 'Nature,' cxvi. p. 897 (1925).

[†] See R. A. Daly, Amer. Jour. Sc. v. p. 349 (1923); and B. Gutenberg, *Der Aufbau der Erde*, p. 52 (1925), for recent discussions of the data.

In 1924, for example, an attempt was made by Gutenberg * to determine the thickness from measurements of surface waves of known period that had traversed the continental crust. Taking :—

T as the thickness of the surface layer ;
c_2 = 3·2 km./sec. as the velocity of distortional waves in the surface layer ;
c_2' = 4·4 km./sec. as the velocity of distortional waves in the substratum ; and
c = 3·8 km./sec. as the velocity of the surface waves having a period of 30 secs. ;

he found T = 30 km. A recomputation by Stoneley gave T = 31·18 km.

Stoneley †, however, drew attention to a serious flaw in the method. He pointed out that, owing to dispersion effects, it is not c, the wave velocity, that is given by the earthquake records, but C, the group velocity. Jeffreys then applied the necessary corrections, and worked out the group velocities for Love waves in a surface layer corresponding to that of the continental crust ‡. He adopted a density of 2·7, and took c_2 = 3·1 km./sec. For the underlying material the corresponding data used were—density = 3·4 ; c_2' = 4·2 km./sec. There is a period for

---

* B. Gutenberg, *Phys. Zeit.* xxv. pp. 377–381 (1924).

† R. Stoneley, M. N. Roy. Astr. Soc., Geophysical Suppl., vol. i. No. 6. p. 280 (Dec. 1925).

‡ H. Jeffreys, M. N. Roy. Astr. Soc., Geophys. Suppl., vol. i. No. 6, p. 282 (Dec. 1925).

which the group velocity of surface waves is a minimum, the value of the latter being just under 3 km./sec. on the data adopted. The corresponding period is approximately 10 secs. These data give T=15·2 km. The adoption of any reasonable figure for the continental density, other than 2·7, which is itself reasonable, would have made no serious difference to the estimate of thickness finally reached.

Applying the same method to other results recorded by Gutenberg [*], one finds that for Eurasia T varies from 10 to 20 km.; and for America from 11 to 19 km. The thickness T=15 km. is therefore a good average. For the sub-oceanic regions a light surface layer ranging from 4 to 8 km. in thickness is indicated. Thus, provided that the densities of 2·7 and 3·4 are justified, the average thickness of the *sial* of the oceanic regions should be about 6 km.

Seismic and thermal evidence have thus again come into close agreement, and for two independent reasons. The 30 km. continent on which Joly founded his theory of the surface history of the earth has become considerably thinner. This conclusion does not, however, invalidate the theory in any way. On the contrary, it relieves the theory of certain embarrassing consequences, and to that extent fortifies it. On the original view developed before the radioactivity of potassium was taken into account, and before the revision of the seismological estimates, cooling of the substratum by conduction through the continents was thought to be of little importance, as the basal temperature was naturally not far from the fusion point of the rocks. With a 15 km. continent, however, the natural temperature of the base is hundreds of degrees below any possible fusion point, and consequently cooling of the substratum through the continents becomes an important process.

VI. *The Nature of the Substratum.*

If we accept an average thickness of 15 km. for the continental crust, and of 6 km. for the surface layer of the ocean floor, it is easy to show from the principle of isostasy that the substratum must everywhere have a density ranging from 3·4 to 3·5 or even a little more. This is not a consequence of the circumstance that Jeffreys adopted 3·4 for the substratum in his work on surface waves. It follows independently from the recognition of the thermal effects due to potassium and the limit which is hereby set to the average continental thickness. Moreover, Jeffreys adopted that particular figure because the velocities of both longitudinal and distortional waves correspond, once they penetrate beyond the lighter crust, to those characteristic of silicate rocks with a density of 3·4 or more *.

---

[*] B. Gutenberg, *Der Aufbau der Erde* (1925), Table 49.

Were the substratum, as Joly and one of the present writers formerly assumed, to have a density of about 3, then continents only 15 km. thick would be submerged beneath an overflow from the oceans. A very much higher substratum density is necessary to give the requisite buoyancy to the continents. One may now picture the surface layer ranging from little or nothing over the sites of the greatest oceanic deeps, to possibly 6 km. thick over the average oceanic regions; rising to 15 km. over the average continental regions, and reaching as much as 30 or 40 km. in regions like the Thibet Plateau and the Himalayas. High-standing areas like the latter can only exist without fusion at the base on the condition that the radioactive content of the underlying column of rocks is unusually low.

The material of the substratum has long been thought by petrologists to be of basaltic composition †. Basaltic lavas have been extruded more often and more abundantly than any other type, and with a striking uniformity of chemical composition ‡. They have, moreover, as already stated, shown no sign of becoming less voluminous during geological time. The parent rocks from which they come must therefore occur in a layer which is very thick compared with the known igneous rocks of basaltic composition. Furthermore, this layer must extend to depths at which the temperature is high enough to permit fusion to occur.

Now there is only one known kind of rock which has the composition of basalt or gabbro and a density of 3·4 or 3·5, and that is *eclogite* §. Thus the assumptions that the substratum is eclogite, a high-pressure facies of basalt, satisfies the isostatic, seismic and petrological data. The only alternative assumption, that the material is peridotite, fails to satisfy the petrological data, for it would leave the basalts of the whole of geological time entirely unexplained. No doubt at a certain depth peridotite comes into place, but a thick eclogite layer must generally intervene between the peridotite of the greater depths and the granitic and related rocks of the surface layer *.

---

* L. H. Adams & E. D. Williamson, Jour. Franklin Inst. cxcv. p. 520 (1923).

† R. A. Daly, 'Igneous Rocks and their Origin,' p. 164 (1914).

‡ H. S. Washington, Bull. Geol. Soc. Amer., vol. 33, p. 797 (1922).

§ L. L. Fermor, Rec. Geol. Surv. India, vol. xliii. p. 41 (1913) P. Eskola, *Norsk. Geol. Tiddsk.* vol. vi. p. 182 (1920-22).

VII. *Geological Time and Latent Heat.*

According to the theory of basaltic cycles, originated by Joly, heat accumulates in the substratum below the level at which the temperature is that of fusion, and so, by supplying latent heat, leads to the production of magma. The latent heat of basaltic material of density 3 is about 270 calories per c.c., and the time taken to supply the whole of this by internal radioactive heating at the rate of $11{\cdot}7 \times 10^{-6}$ calorie per year would evidently be about 23 million years. Joly † has attempted to apply a simple calculation of this sort to the problem of geological time, and since he took into consideration only uranium and thorium he naturally arrived at a longer estimate of the time required to supply the latent heat. Unfortunately, the method seems unlikely ever to lead to acceptable results for two reasons. We have now to consider the latent heat not of basalt or gabbro, but of their high-pressure equivalent, eclogite; and not merely of eclogite as we occasionally encounter it near the earth's surface, but eclogite at a pressure of thousands of atmospheres. Moreover, it seems somewhat improbable that exactly *all* the eclogite of the zone of fusion should become liquid during a single cycle. When half the latent heat has been supplied, half of the material will have changed to the liquid state ; and as the magma rises, as it must do, into the zone of cooling above, it may consolidate and die out long before the rest of the substratum has altogether fused.

The amount of magma produced depends not only on the supply of latent heat, but on the thickness of the zone through which it is being supplied, and also on the rate at which it rises, by a process of crystal stoping into the cooler regions above. Indeed, the magma rises because the crystal debris liberated from the roof by corrosion along the crystal boundaries falls to the bottom and so displaces the liquid upwards. The magma is therefore always underlain by solid material (unless, exceptionally, the peridotite of still greater depths also becomes fluid and engulfs that material), and consequently there is always being generated a certain supply of magma. It is the ascent and consolidation of the accumulated magma that gives rise to the periodicity ; and each cycle consists of a period of magma accumulation and ascent, followed by a period of cooling and the consequent descent of the level beneath which magma can form.

---

* Except possibly at certain times in the earth's history when the peridotite below may have fused and risen through the eclogite. Such a condition would be unstable, for later the eclogite would fuse and rise again above the peridotite. See A. Holmes, Geol. Mag., July, 1926, p. 326.

† J. Joly, 'The Surface History of the Earth,' pp. 90–92 and 153 (1925).

The process may be capable of mathematical treatment in such a way as to give an expression for time in terms of other quantities, but the latter involve matters on which we have absolutely no data. The thickness of the eclogite zone, for example, is not likely to be revealed by seismic evidence, because the density is practically identical with that of peridotite, and no significant difference in elastic constants is to be anticipated. Thus, as already stated in a former publication*, there are good reasons for considering "that far-reaching hypotheses of this kind should not be regarded as providing any sort of method for estimating geological time, but should themselves be tested, and modified where necessary, by reference to the ascertained data of geological time-measurements."

VIII. *Conclusions.*

(*a*) The velocities of the β-rays emitted by rubidium and potassium are respectively $0{\cdot}60\,c$ and $0{\cdot}85\,c$. The corresponding kinetic energies are respectively $2{\cdot}04 \times 10^{-7}$ and $7{\cdot}30 \times 10^{-7}$ erg.

(*b*) On available data, the most probable half-value period of rubidium is $T_{Rb} = 10^{11}$ years, and of potassium $T_K = 1{\cdot}5 \times 10^{12}$ years. The disintegration constants are $\lambda_{Rb} = 6{\cdot}9 \times 10^{-12}$ year^{-1} for rubidium, and $\lambda_K = 4{\cdot}6 \times 10^{-13}$ year^{-1} for potassium.

(*c*) As an emitter of radio-thermal energy in rocks, potassium is, in the aggregate, of the same order of importance as uranium or thorium.

---

* A. Holmes, Phil. Mag. (7) i. p. 1072 (1926).

(*d*) The radioactivity of rubidium has no geological significance, on account of the rarity of the element.

(*e*) There is no reason to suppose that as much as one per cent. of the energy of radioactive rays (from whatever source) can be expended in any other way than by conversion into heat.

(*f*) The continental crust must be less than 30 km., and probably does not exceed 20 km. in average thickness, a result that agrees with a recent estimate of 15 km. due to Jeffreys.

(*g*) The substratum beneath the continents and the surface layer of the ocean floor are shown to consist most probably of eclogite, a high-pressure facies of basaltic rock, having a density of 3·4 to 3·5.

(*h*) The time required for the accumulation of the latent heat of the material of the substratum may be about 23 million years, but this result is of theoretical interest only, and provides at present no basis for the erection of a geological time-scale.

June 21, 1926.

Note added Nov. 1, 1926.—Since this paper was written, further information has become available bearing on the thickness and structure of the continental masses. The following communications should therefore be referred to. They point to an average continental thickness ranging from 20 km. to 30 km., the lower estimate being preferable for thermal reasons; and to a downward distribution of rock-types tentatively interpreted by Jeffreys as granite-basaltic glass-dunite; and alternatively interpreted by one of us (A. H.) as granite-diorite-eclogite-dunite.

A. Holmes: "Contributions to the Theory of Magmatic Cycles." Geol. Mag., July 1926, p. 306.

L. H. Adams and R. E. Gibson: "The Compressibilities of Dunite and of Basalt Glass and their Bearing on the Composition of the Earth." Proc. Nat. Acad. Sci. xii. p. 275 (1926).

H. Jeffreys: "The Structure of the Continents." 'Nature,' Sept. 25, 1926. p. 443.

A. Holmes: *Ibid.* Oct. 23, 1926, p. 586.

The Presidential Address by Dr. J. W. Evans, which was cited in Section IV., has now been published in the Q. J. G. S. lxxxii. p. 60 (1926).

CXVIII. *On the Stresses in a Spoked Wheel under Loads applied to the Rim.* *By* Professor A. J. Sutton Pippard, *M.B.E., D.Sc., and* J. F. Baker, *B.A., University College, Cardiff*[*].

ONE of the commonest units employed in engineering construction is the wheel, consisting of a rim connected to a central boss or hub by a number of evenly spaced arms or spokes. In general these spokes are rigidly attached both to the rim and to the hub. In consequence, the analysis of the stresses in such a wheel is a matter of considerable importance, and while solutions have been obtained for certain particular cases[†] of loading, it does not appear that the general problem has received the attention which its interest and importance merits.

In the present paper is given an analysis of the stresses in such a wheel when it is held rigidly at the hub and subjected to any system of loads applied to the rim. Since the effects produced by a number of loads can be found by superimposing those due to the loads considered separately, it is only necessary to analyse the case of a single load, and this in turn can be considered as two loads, one acting tangentially and the other acting radially. The problem is therefore reduced to the analysis of the stresses under a tangential and a radial load, and these cases are considered separately.

The results obtained appear somewhat complex: this, in view of the general nature of the problem, is unavoidable, but the actual computation in any particular case, although somewhat long, is not difficult. It is necessary, however, to work to a considerable degree of accuracy.

Figure 1 indicates the type of wheel considered.

Let N = number of arms evenly spaced.

2θ = angle between arms.

R = radius of rim measured to the centroid of its section.

R_0 = radius of hub.

I = moment of inertia of the cross-section of the rim about its axis of bending.

---

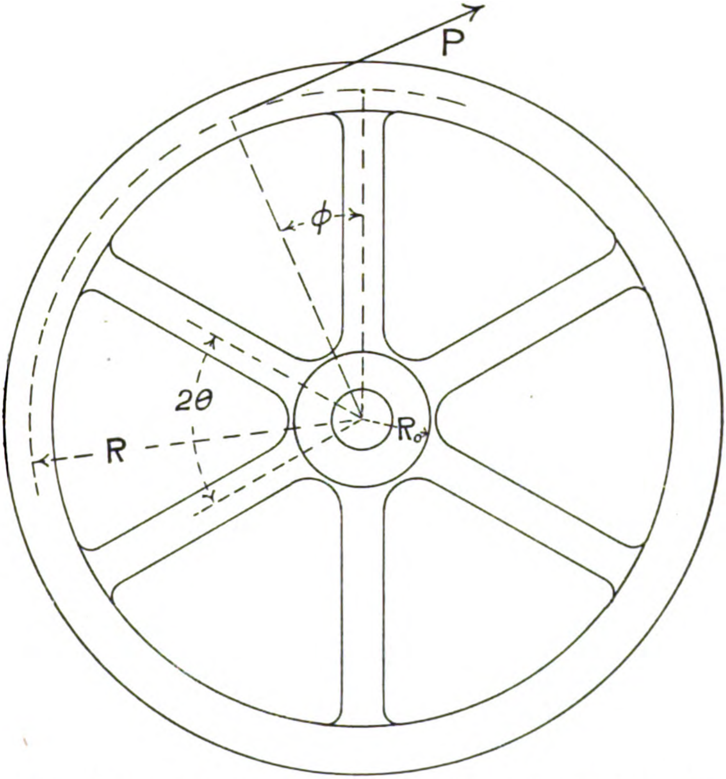
[*] Communicated by the Authors.

[†] *Cp.* "Stresses in the rim and arms of a Flywheel rotating at constant speed," J. Longbottom: Trans. Inst. of Engineers and Shipbuilders of Scotland, lxii. (1919). "Stresses in a uniformly rotating Flywheel," A. J. S. Pippard: Inst. Mech. Engs., Jan. 1924. "Stresses in a Flywheel due to acceleration," A. J. S. Pippard: Inst. Mech. Engs., Jan. 1926.

I_a = moment of inertia of cross-section of an arm about its axis of bending.
a = area of cross-section of rim.
a_0 = area of cross-section of an arm.
E = modulus of elasticity of material of rim and arm.

The method of solution adopted is to consider the wheel as a framework with a number of redundant reactions and to apply the Principle of Least Work to obtain the necessary equations.

Fig. 1.



The frame contains 2N nodes, and so the number of bars required to make it just stiff is 4N−3. If the segments of the rim and the arms were pinjointed together and the arms pinned to the hub, the number of bars provided would be 2N. Since the N nodes on the hub are fixed relatively to each other the hub itself is equivalent to (2N−3) members and could be replaced by this number of bars

Hence the effective number of bars provided in the pinned framework is (4N − 3), *i.e.* such a wheel would be just stiff. The continuity of the rim over the arms introduces one "redundancy" at each point, and since the arms are rigidly fixed to the rim and the hub, these attachments introduce two "redundancies" more for each arm. Hence the total number of "redundancies" in the frame is 3N.

In fig. 2 let the reactions between the arms and the hub consist of

Forces $H_1, H_2 \ldots H_N$ tangential to the hub,

Forces $T_1, T_2 \ldots T_N$ acting along the arms,

Moments $M_1, M_2 \ldots M_N$.

We shall treat $H_1 \ldots H_{N-1}$, $T_1 \ldots T_{N-1}$, and $M_1 \ldots M_{N-1}$ as "redundancies," giving 3(N − 1) of the total number present. H_N, T_N, and M_N are then determinate from the conditions of static equilibrium.

The remaining three "redundancies" are conveniently taken to be the resultant actions at a section of the rim just to the right of the Nth arm. These consist of a radial force V_0, a tangential force H_0, and a couple M_0.

There are then 3(N + 1) unknown forces and couples to be determined. Three of the essential equations are provided by a consideration of the static equilibrium of the wheel and the remaining 3N by application of the Principle of Least Work as follows:—

Let U be the total strain energy of the wheel.

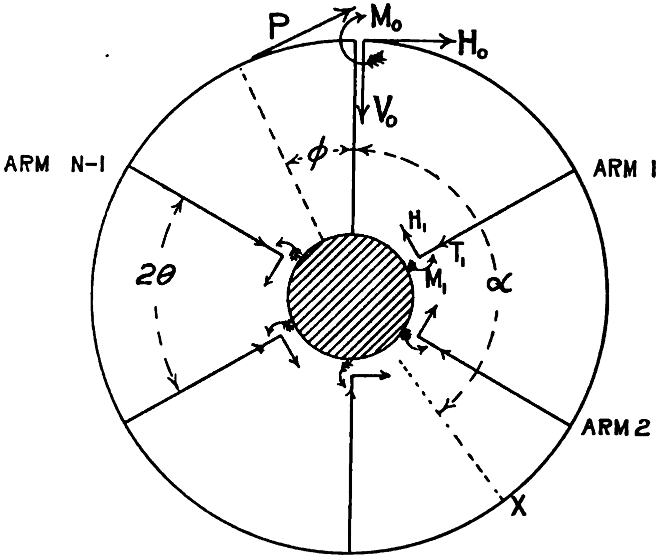
Then:

$$\left.\begin{array}{r}
\dfrac{\partial U}{\partial H_0} = 0, \\[2ex]
\dfrac{\partial U}{\partial V_0} = 0, \\[2ex]
\dfrac{\partial U}{\partial M_0} = 0, \\[2ex]
\dfrac{\partial U}{\partial H_1} = \dfrac{\partial U}{\partial H_2} = \ldots\ldots\ldots\ldots \dfrac{\partial U}{\partial H_{N-1}} = 0, \\[2ex]
\dfrac{\partial U}{\partial T_1} = \dfrac{\partial U}{\partial T_2} = \ldots\ldots\ldots\ldots \dfrac{\partial U}{\partial T_{N-1}} = 0, \\[2ex]
\dfrac{\partial U}{\partial M_1} = \dfrac{\partial U}{\partial M_2} = \ldots\ldots\ldots\ldots \dfrac{\partial U}{\partial M_{N-1}} = 0.
\end{array}\right\} \quad . \quad . \quad (1)$$

Case I.—Tangential load on rim.

In fig. 2 let P be a tangential force acting on the rim between the (N−1)th and Nth arms, and let its point of application be at an angular distance ϕ from the Nth arm.

Fig. 2.



Resolving forces perpendicular to, and along this arm and taking moments about the centre of the wheel, the conditions for static equilibrium are obtained as follows :—

$$(H_1 \cos 2\theta + H_2 \cos 4\theta \ldots + H_N \cos 2N\theta) + (T_1 \sin 2\theta + T_2 \sin 4\theta \ldots + T_{N-1} \sin 2(N-1)\theta) = P \cos\phi, \quad . \quad . \quad . \quad (2)$$

$$-(H_1 \sin 2\theta + H_2 \sin 4\theta \ldots + H_{N-1} \sin 2(N-1)\theta) + (T_1 \cos 2\theta + T_2 \cos 4\theta \ldots + T_N \cos 2N\theta) = P \sin\phi, \quad . \quad (3)$$

$$R_0(H_1 + H_2 \ldots + H_N) + (M_1 + M_2 \ldots + M_N) = PR. \quad . \quad . \quad (4)$$

Under the action of P the rim and arms of the wheel are subjected to bending, axial loads and shearing forces, all of which contribute to the strain energy. The effect of shearing force is, however, negligible compared with the others, and, following the usual custom, the strain energy due to bending and direct tension or compression will alone be considered.

The hub will be assumed to be rigid and will therefore contribute nothing to the strain energy. Also, in writing down the strain energy, the effect of the initial curvature of the rim will be neglected. The extra terms which would be involved would needlessly complicate the equations and their effect is entirely unimportant.

Let X be any point on the rim between the pth and $(p+1)$th arms, and let the angle between the radius to X and the Nth arm be α.

When $\alpha < (2\pi - \phi)$ the compressive tangential force in the rim at X is

$$\begin{aligned} T_x = {} & H_0 \cos\alpha + V_0 \sin\alpha \\ & - \{H_1 \cos(\alpha - 2\theta) + H_2 \cos(\alpha - 4\theta) \ldots H_p \cos(\alpha - 2p\theta)\} \\ & + \{T_1 \sin(\alpha - 2\theta) + T_2 \sin(\alpha - 4\theta) \ldots T_p \sin(\alpha - 2p\theta)\}. \qquad (5) \end{aligned}$$

When $\alpha > (2\pi - \phi)$ an extra term $P\cos(\alpha + \phi)$ must be added.

When $\alpha < (2\pi - \phi)$ the bending moment in the rim at X is

$$\begin{aligned} M_x = {} & M_0 + H_0 R(1 - \cos\alpha) - V_0 R \sin\alpha \\ & + R\{H_1 \cos(\alpha - 2\theta) + H_2 \cos(\alpha - 4\theta) \ldots H_p \cos(\alpha - 2p\theta)\} \\ & - R\{T_1 \sin(\alpha - 2\theta) + T_2 \sin(\alpha - 4\theta) \ldots T_p \sin(\alpha - 2p\theta)\} \\ & - R_0\{H_1 + H_2 \ldots H_p\} - \{M_1 + M_2 \ldots M_p\}. \qquad (6) \end{aligned}$$

When $\alpha > (2\pi - \phi)$ an extra term $PR(1 - \cos(\alpha + \phi))$ must be added.

Then the value of $\frac{\partial U}{\partial M_0}$ for the segment of rim between $\alpha = 2p\theta$ and $\alpha = 2(p+1)\theta$ is

$$\frac{R}{EI}\int_{2p\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial M_0} \cdot d\alpha,$$

and for the whole wheel, since the energy of the arms does not involve the terms M_0, H_0, and V_0,

$$\frac{\partial U}{\partial M_0} = \sum_{p=0}^{p=N-1} \frac{R}{EI}\int_{2p\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial M_0} \cdot d\alpha = 0.$$

Similarly,

$$\frac{\partial U}{\partial H_0} = \sum_{p=0}^{p=N-1} \left[\frac{R}{EI}\int_{2p\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial H_0} \cdot d\alpha + \frac{R}{aE}\int_{2p\theta}^{2(p+1)\theta} T_x \cdot \frac{\partial T_x}{\partial H_0} \cdot d\alpha\right] = 0$$

and

$$\frac{\partial U}{\partial V_0} = \sum_{p=0}^{p=N-1} \left[\frac{R}{EI}\int_{2p\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial V_0} d\alpha + \frac{R}{aE}\int_{2p\theta}^{2(p+1)\theta} T_x \cdot \frac{\partial T_x}{\partial V_0} \cdot d\alpha\right] = 0$$

On integrating and summing these expressions after substituting the values of M_x, T_x, etc., we obtain equations (7), (8), and (9).

In these equations we write

$$A = \frac{R^2}{EI},$$

$$B = \frac{1}{aE},$$

$$C = \frac{L^2}{EI_a},$$

$$D = \frac{1}{a_0E},$$

$$L = (R-R_0).$$

$$\begin{aligned} &2\pi(M_0+RH_0)-R(T_1+T_2\ldots T_N) \\ &\qquad +2\theta\{R_0(H_1+2H_2+3H_3\ldots NH_N)+(M_1+2M_2\ldots NM_N)\} \\ &\qquad -PR(2\pi-\phi)=0. \qquad (7) \end{aligned}$$

$$\begin{aligned} &(A+B)\left[\pi RH_0+\frac{R}{2}\{H_1\sin 2\theta+H_2\sin 4\theta\ldots H_{N-1}\sin 2(N-1)\theta\}\right. \\ &\qquad +R\theta\{(H_1\cos 2\theta+2H_2\cos 4\theta\ldots NH_N) \\ &\qquad\qquad +(T_1\sin 2\theta+2T_2\sin 4\theta\ldots(N-1)T_{N-1}\sin 2(N-1)\theta)\} \\ &\qquad \left.-\frac{PR}{2}\{(2\pi-\phi)\cos\phi-\sin\phi\}\right] \\ &\quad -A\left[\{M_1\sin 2\theta+M_2\sin 4\theta\ldots M_{N-1}\sin 2(N-1)\theta\}\right. \\ &\qquad +R_0\{H_1\sin 2\theta+H_2\sin 4\theta\ldots H_{N-1}\sin 2(N-1)\theta\} \\ &\qquad \left.+PR\sin\phi\right]=0. \qquad (8) \end{aligned}$$

$$\begin{aligned} &(A+B)\left[\pi RV_0+\frac{R}{2}\{T_1\sin 2\theta+T_2\sin 4\theta\ldots T_{N-1}\sin 2(N-1)\theta\}\right. \\ &\qquad +R\theta\{H_1\sin 2\theta+2H_2\sin 4\theta\ldots(N-1)H_{N-1}\sin 2(N-1)\theta) \\ &\qquad\qquad -(T_1\cos 2\theta+2T_2\cos 4\theta\ldots NT_N)\} \\ &\qquad \left.+\frac{PR}{2}(2\pi-\phi)\sin\phi\right] \\ &\quad +A\left[\{M_1\cos 2\theta+M_2\cos 4\theta\ldots M_N\}\right. \\ &\qquad \left.+R_0\{H_1\cos 2\theta+H_2\cos 4\theta\ldots H^N\}-PR\cos\phi\right]=0. \qquad (9) \end{aligned}$$

The three groups of equations obtained by differentiating the strain energy with respect to $H_1 \ldots H_{N-1}$, $T_1 \ldots T_{N-1}$, and $M_1 \ldots M_{N-1}$ must now be considered. To form these equations we write down

$$\frac{\partial U}{\partial H_r}=0, \quad \frac{\partial U}{\partial T_r}=0, \quad \text{and} \quad \frac{\partial U}{\partial M_r}=0,$$

and then by giving r all values from $r=1$ to $r=(N-1)$ inclusive all the required equations are obtained.

Since the bending and direct loads in the rth and Nth arms are functions of M_r, H_r, and T_r the strain energy of these arms will appear in the value of U.

Then

$$\frac{\partial U}{\partial M_r}=\frac{1}{EI_a}\int_0^L\left(m_r\cdot\frac{\partial m_r}{\partial M_r}+m_n\cdot\frac{\partial m_n}{\partial M_r}\right)\cdot dx$$
$$+\sum_p \frac{R}{EI}\int_{2p\theta}^{2(p+1)\theta} M_x\cdot\frac{\partial M_x}{\partial M_r}\cdot d\alpha,$$

where m_r and m_n are the bending moments at any point in the rth and Nth arms respectively, so that $m_r=M_r-H_rx$, where x is measured from the point where the arm joins the hub.

The second integral relates to the segment of the rim between the pth and $(p+1)$th arms, and after evaluation the terms composing it must be summed appropriately as follows:—

Terms in M_0, H_0, and V_0 from $p=r$ to $p=(N-1)$.
Terms in M_q, T_q, and H_q where $q \leqq r$ from $p=r$ to $p=(N-1)$
and where $q>r$ from $p=q$ to $p=(N-1)$.

In a similar manner we may write

$$\frac{\partial U}{\partial H_r}=\frac{1}{EI_a}\int_0^L\left(m_r\cdot\frac{\partial m_r}{\partial H_r}+m_n\cdot\frac{\partial m_n}{\partial H_r}\right)dx+\frac{1}{a_0E}\int_0^L T_N\cdot\frac{\partial T_N}{\partial H_r}\cdot dx$$
$$+\sum_p\left[\frac{R}{EI}\int_{2p\theta}^{2(p+1)\theta} M_x\cdot\frac{\partial M_x}{\partial H_r}\cdot d\alpha+\frac{1}{aE}\int_{2p\theta}^{2(p+1)\theta} T_x\cdot\frac{\partial T_x}{\partial H_r}\cdot d\alpha\right]$$

and

$$\frac{\partial U}{\partial T_r}=\frac{1}{EI_a}\int_0^L\left(m_n\cdot\frac{\partial m_n}{\partial T_r}\right)dx+\frac{1}{a_0E}\int_0^L\left(T_r+T_N\cdot\frac{\partial T_N}{\partial T_r}\right)\cdot dx$$
$$+\sum_p\left[\frac{R}{EI}\int_{2\theta}^{2(p+1)\theta} M_x\cdot\frac{\partial M_x}{\partial T_r}\cdot d\alpha+\frac{1}{aE}\int_{2\theta}^{2(p+1)} T_x\cdot\frac{\partial T_x}{\partial T_r}\cdot d\alpha\right].$$

Upon substituting and integrating, and summing these expressions the equations (10), (11), and (12) are obtained, where

$$\alpha_r = 2M_r - H_rL,$$

$$\alpha_n = 2M_N - H_NL,$$

$$\beta_r = 3M_r - 2H_rL,$$

$$\beta_n = 3M_N - 2H_NL, \quad \text{etc.}$$

$$A\Big[2(N-r)\theta M_0 + H_0R\{2(N-r)\theta + \sin 2r\theta\} + V_0R\{1-\cos 2r\theta,$$

$$+ R\sin 2r\theta \sum_{q=r}^{q=N} (H_q\cos 2q\theta + T_q\sin 2q\theta)$$

$$+ R\cos 2r\theta \sum_{q=r}^{q=N} (T_q\cos 2q\theta - H_q\sin 2q\theta) - R\sum_{q=r}^{q=N} T_q$$

$$+ 2\theta \sum_{q=1}^{q=N-r} q(M_{r+q} + R_0H_{r+q})$$

$$-PR\{\sin(2r\theta+\phi) + 2(N-r)\theta - \phi\}\Big] + \frac{CR}{2L}(\alpha_n - \alpha_r) = 0. \quad . \quad . \quad . \quad (10)$$

$$(A+B)\Big[\frac{H_0R}{2}\{\sin 2r\theta + 2r\theta\cos 2r\theta\} + V_0R(r\theta\sin 2r\theta)$$

$$-\frac{R}{2}\sum_{q=1}^{q=r-1} H_q\sin 2(r-q)\theta$$

$$+R\theta\sum_{q=1}^{q=r-1}(r-q)\{T_q\sin 2(r-q)\theta - H_q\cos 2(r-q)\theta\}\Big]$$

$$+A\Big[-(M_0+H_0R)\sin 2r\theta + \sum_{q=1}^{q=r-1}(R_0H_q + M_q(\sin 2(r-q)\theta\Big]$$

$$+\frac{C}{6}(\beta_n\cos 2r\theta - \beta_r)$$

$$-\frac{CR_0}{2L}(\alpha_r - \alpha_n\cos 2r\theta) + LDT_N\sin 2r\theta = 0. \quad . \quad . \quad (11)$$

$$(A+B)\Big[H_0R(r\theta\sin 2r\theta) + \frac{V_0R}{2}\{\sin 2r\theta - 2r\theta\cos 2r\theta\}$$

$$+\frac{R}{2}\sum_{q=1}^{q=r-1} T_q\sin 2(r-q)\theta$$

$$-R\theta\sum_{q=1}^{q=r-1}(r-q)\{H_q\sin 2(r-q)\theta + T_q\cos 2(r-q)\theta\}\Big]$$

$$-A\Big[(M_0+H_0R)(1-\cos 2r\theta)$$

$$-\sum_{q=1}^{q=r-1}(R_0H_q+M_q)(1-\cos 2(r-q)\theta)\Big] + \frac{C}{6}(\beta_n\sin 2r\theta)$$

$$+\frac{CR_0}{2L}\alpha_n\sin 2r\theta + LD(T_r - T_n\cos 2r\theta) = 0. \quad . \quad . \quad (12$$

The reduction of these equations to a useful form is a rather long process, but by operating with (10), (11), and (12) and the corresponding equations obtained when r is replaced by $(r+1)$, the results given in (13), (14), and (15) are obtained.

$$\begin{aligned}
&\alpha_{r+1}-\alpha_r\\
&\quad=\frac{2AL}{CR}\Big[-2\theta(M_0+H_0R)+H_0R\{\sin 2(r+1)\theta-\sin 2r\theta\}\\
&\qquad\qquad+V_0R\{\cos 2r\theta-\cos 2(r+1)\theta\}\\
&\quad+2\theta\sum_{q=1}^{q=r}(M_q+R_0H_q)+2R\sin\theta\sum_{q=1}^{q=r}\{T_q\sin(2r-2q+1)\theta\\
&\qquad\qquad-H_q\cos(2r-2q+1)\theta\}\Big].
\end{aligned}$$

$$\begin{aligned}
&T_{r+1}-T_r\cos 2\theta \qquad . \quad . \quad . \qquad (13)\\
&\quad=\frac{A+B}{2LD}\Big[H_0R\{\sin 2\theta\sin 2r\theta-2\theta\sin 2(r+1)\theta\}\\
&\qquad\qquad+V_0R\{2\theta\cos 2(r+1)\theta-\sin 2\theta\cos 2r\theta\}\\
&\quad+2R\theta\sum_{q=1}^{q=r}\{H_q\sin 2(r-q+1)\theta+T_q\cos 2(r-q+1)\theta\}\\
&\qquad-R\sin 2\theta\sum_{q=1}^{q=r}\{T_q\cos 2(r-q)\theta+H_q\sin 2(r-q)\theta\}\\
&\quad-\frac{R}{2}\{T_r\sin 2\theta+H_r\cos 2\theta\}\Big]\\
&\qquad+\frac{A}{LD}\Big[(M_0+H_0R)-\sum_{q=1}^{q=r}(M_q+R_0H_q)\Big](1-\cos 2\theta)\\
&\qquad-\frac{C}{6LD}\beta_r\sin 2\theta-\frac{CR_0}{2L^2D}.\,\alpha_r\sin 2\theta. \quad . \quad . \quad . \qquad (14)
\end{aligned}$$

$$\begin{aligned}
&\beta_{r+1}-\beta_r\cos 2\theta\\
&\quad=\frac{3(A+B)}{C}\Big[H_0R\{\sin 2\theta\cos 2r\theta+2\theta\cos 2(r+1)\theta\}\\
&\qquad\qquad+V_0R\{2\theta\sin 2(r+1)\theta+\sin 2\theta\sin 2r\theta\}\\
&\quad+2R\theta\sum_{q=1}^{q=r}\{T_q\sin 2(r-q+1)\theta-H_q\cos 2(r-q+1)\theta\}\\
&\qquad+R\sin 2\theta\sum_{q=1}^{q=r}\{T_q\sin 2(r-q)\theta-H_q\cos 2(r-q)\theta\}\\
&\quad+\frac{R}{2}\{T_r\cos 2\theta-H_r\sin 2\theta\}\Big]\\
&\qquad-\frac{6A}{C}\Big[(M_0+H_0R)-\sum_{q=1}^{q=r}(M_q+R_0H_q)\Big]\sin 2\theta\\
&\qquad+\frac{6LD}{C}T_r\sin 2\theta-\frac{3R_0}{L}(\alpha_{r+1}-\alpha_r\cos 2\theta) \quad . \qquad (15)
\end{aligned}$$

In order that the difference equations (13), (14), and (15) can be used it is necessary to determine values for α_1, β_1, and T_1. If, in equations (10), (11), and (12) r is put equal to unity, the resulting expressions can be reduced to simple forms by the use of equations (7), (8), and (9) and we obtain

$$\alpha_1 = \frac{2AL}{CR}\left[-2\theta(M_0+H_0R)+H_0R\sin 2\theta\right. \cdot$$

$$\left.+V_0R(1-\cos 2\theta)\right]+\alpha_n. \quad (16)$$

$$\beta_1 = \frac{6(A+B)}{C}\left[\frac{H_0R}{2}\sin 2\theta+H_0R\theta\cos 2\theta+V_0R\theta\sin 2\theta\right]$$

$$-\frac{6A}{C}\sin 2\theta\,[M_0+H_0R]$$

$$-\frac{3R_0}{L}(\alpha_1-\alpha_n\cos 2\theta)+\beta_n\cos 2\theta+\frac{6LD}{C}(T_N\sin 2\theta). \quad (17)$$

$$T_1 = -\frac{A+B}{LD}\left[H_0R\theta\sin 2\theta-V_0R\theta\cos 2\theta+\frac{V_0R}{2}\sin 2\theta\right]$$

$$+\frac{A}{LD}(1-\cos 2\theta)[M_0+H_0R]$$

$$-\frac{C}{6LD}\cdot\beta_n\sin 2\theta-\left(\frac{CR_0}{2L^2D}\cdot\sin 2\theta\right)\alpha_n+T_N\cos 2\theta. \quad (18)$$

These equations give α_1, β_1, and T_1 in terms of the unknown quantities M_0, H_0, V_0, α_N, β_N, and T_N, and having found them we have

$$H_1L=(3\alpha_1-2\beta_1) \quad \text{and} \quad M_1=(2\alpha_1-\beta_1).$$

Equations (13), (14), and (15) can now be used, since if we put $r=1$ we obtain α_2, β_2, and T_2 in terms of the same six quantities, and so H_2 and M_2.

Successive substitution up to $r=(N-2)$ enables all the quantities $T_1, \ldots T_{N-1}$, $H_1 \ldots H_{N-1}$, and $M_1 \ldots M_{N-1}$ to be found in terms of M_0, α_n, etc.

The static equations (2), (3), and (4) and the equations (7), (8), and (9) can now be used to furnish solutions for M_0, H_0, V_0, T_N, H_N, and M_N.

The equations so far obtained are perfectly general and may be used for the determination of the stress distribution in any wheel. The arithmetical work is rather long, but further simplification of the equations does not appear to be practicable and in any case does not lessen the labour of computation.

There are, however, two limiting cases which deserve attention, viz. the case of a rigid rim and the case of rigid arms.

Wheel in which the rim is rigid.

When the rim is rigid A=B=0, so that

$$\alpha_1 = \alpha_2 = \ldots\ldots = \alpha_n.$$

And

$$\beta_1 = -\frac{3R_0}{L}(1-\cos 2\theta)\alpha_n + \beta_n \cos 2\theta + \frac{6LD}{C} T_N \sin 2\theta,$$

$$\beta_r = -\frac{3R_0}{L}(1-\cos 2r\theta)\alpha_n + \beta_n \cos 2r\theta + \frac{6LD}{C} T_N \sin 2r\theta.$$

While

$$T_1 = -\left(\frac{C}{6LD}\sin 2\theta\right)\beta_n - \left(\frac{CR_0}{2L^2D}\sin 2\theta\right)\alpha_n + T_N \cos 2\theta,$$

$$T_r = -\left(\frac{C}{6LD}\sin 2r\theta\right)\beta_n - \left(\frac{CR_0}{2L^2D}\sin 2r\theta\right)\alpha_n + T_N \cos 2r\theta.$$

Therefore

$$M_r = (2\alpha_r - \beta_r) = 2\alpha_n + \frac{3R_0}{L}(1-\cos 2r\theta)\alpha_n - \beta_n \cos 2r\theta - \frac{6LD}{C} T_N \sin 2r\theta$$

and

$$H_r = \frac{1}{L}\{3\alpha_r - 2\beta_r\} = \frac{1}{L}\left\{3\alpha_n + \frac{6R_0}{L}(1-\cos 2r\theta)\alpha_n - 2\beta_n \cos 2r\theta - \frac{12LD}{C} T_N \sin 2r\theta\right\}.$$

Using the static conditions in equations (2), (3), and (4) it is found that

$$H_N = P\cos\phi + \alpha_n\left\{\frac{3}{L} + \frac{3R_0N}{L^2} + \frac{CR_0N}{4L^2D}\right\} + \beta_n\left\{\frac{N-2}{L} + \frac{CN}{12LD}\right\},$$

$$T_N = P\sin\phi - T_N\left\{\frac{6DN}{C} + \frac{N-2}{2}\right\},$$

$$M_N = P(R - R_0\cos\phi) - \alpha_n\left\{\frac{R_0^2N}{L^2}\left(9 + \frac{C}{4D}\right) + \frac{6R_0N}{L} + 2(N-1)\right\} - \beta_n\left\{\frac{R_0N}{L}\left(1 + \frac{C}{12D}\right) + 1\right\}.$$

And from these results

$$\alpha_n = \frac{PR}{\frac{2R_0N}{L}\left(3+\frac{3R_0}{L}+\frac{L}{R_0}\right)},$$

$$\beta_n = -\frac{3P}{N}\left[\frac{L\cos\phi}{\left(3+\frac{C}{4D}\right)}+\frac{R}{2\left(3+\frac{3R_0}{L}+\frac{L}{R_0}\right)}\right],$$

$$T_N = \frac{2P\sin\phi}{N\left(1+\frac{12D}{C}\right)}.$$

Now C is generally very large compared with D, so that we can put

$$\beta_n \doteqdot -\frac{3P}{N}\left[\frac{L\cos\phi}{\frac{C}{4D}}+\frac{R}{2\left(3+\frac{3R_0}{L}+\frac{L}{R_0}\right)}\right].$$

Then substituting for α_n, β_n, and T_N, we find that approximately

$$T_r = \frac{2P}{N}\{\sin(2r\theta+\phi)\}.$$

This is a maximum when $\sin(2r\theta+\phi)$ is a maximum, *i. e.* when $(2r\theta+\phi)=\frac{\pi}{2}$ or $\frac{3\pi}{2}$.

Hence the maximum value of the tension in an arm occurs when ϕ is such as to make the load act parallel to an arm, and the maximum value of T is then $\frac{2P}{N}$.

If the wheel has an even number of arms there will simultaneously occur an equal compression in the opposite arm to that carrying the maximum tension.

Again, it is found that

$$M_r = \frac{PR}{2N}\left[\frac{\frac{2L}{R_0}+3}{3+\frac{3R_0}{L}+\frac{L}{R_0}}\right]+\frac{12PDL}{CN}[\cos(2r\theta+\phi)],$$

which is a maximum when $\cos(2r\theta+\phi)$ is a maximum.

This occurs when $\phi=0$ and $r=N$, *i. e.* when the load is applied at the end of one arm, and the value of M is then

$$M_{\max.} = \frac{PR}{2N}\left[\frac{\frac{2L}{R_0}+3}{\left(3+\frac{3R_0}{L}+\frac{L}{R_0}\right)}\right]+\frac{12PLD}{NC}.$$

Similarly,

$$H_r = \frac{3PR}{2NL}\left[\frac{\frac{L}{R_0}+2}{\left(3+\frac{3R_0}{L}+\frac{L}{R_0}\right)}\right]+\frac{24PD}{CN}\cos(2r\theta+\phi);$$

this is also a maximum when the load is applied to the end of one arm and

$$H_{\text{max.}} = \frac{3PR}{2NL}\left[\frac{\frac{L}{R_0}+2}{\left(3+\frac{3R_0}{L}+\frac{L}{R_0}\right)}\right]+\frac{24PD}{CN}$$

Wheel in which the arms are rigid.

When the arms are rigid and the rim is elastic any load P placed between the (N−1)th and Nth arms will cause stresses only in these two arms.

Hence

$$T_1 = T_2 = \dots T_{N-2} = 0,$$
$$M_1 = M_2 = \dots M_{N-2} = 0,$$
$$H_1 = H_2 = \dots H_{N-2} = 0.$$

The static equations (2), (3), and (4) then give

$$H_N = P\cos\phi - H_{N-1}\cos 2\theta + T_{N-1}\sin 2\theta,$$
$$T_N = P\sin\phi - T_{N-1}\cos 2\theta - H_{N-1}\sin 2\theta,$$
$$M_N = PR - M_{N-1} - R_0\{H_{N-1}(1-\cos 2\theta) + T_{N-1}\sin 2\theta + P\cos\phi\}.$$

Also, since M_0, V_0, and H_0 are all zero, we have, on substituting the values of H_N, T_N, and M_N in (7), (8), and (9), the equations

$$H_{N-1}\left(\frac{R}{2}\sin 2\theta + R\theta\cos 2\theta - R_0\sin 2\theta\right) - T_{N-1}(R\theta\sin 2\theta) - M_{N-1}\sin 2\theta + \frac{PR}{2}(\sin\phi - \phi\cos\phi) = 0.$$

$$H_{N-1}\{R_0(1-\cos 2\theta) - R\theta\sin 2\theta\} + T_{N-1}\left\{\frac{R}{2}\sin 2\theta - R\theta\cos 2\theta\right\} + M_{N-1}(1-\cos 2\theta) + \frac{PR}{2}\{\phi\sin\phi - 2(1-\cos\phi)\} = 0.$$

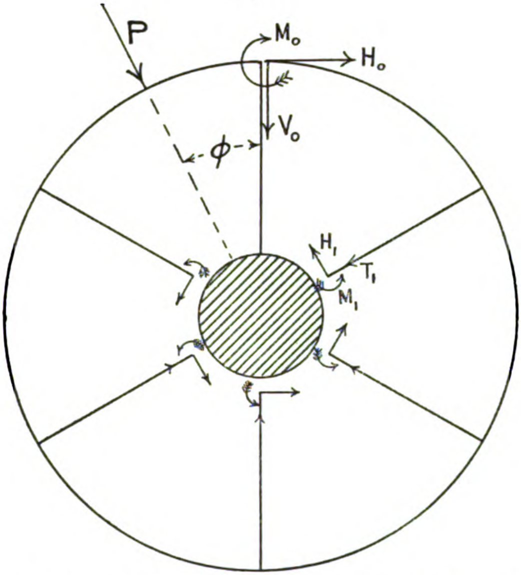
$$H_{N-1}\{2\theta R_0 - R\sin 2\theta\} + T_{N-1}\{R(1-\cos 2\theta)\} + 2\theta M_{N-1} + PR(\sin\phi - \phi) = 0.$$

The general solution of these is rather long, but for any special case the coefficients of H_{N-1}, T_{N-1}, and M_{N-1} are easily found and the particular solution readily obtained. H_N, T_N, and M_N are then found from the static conditions.

Case 2.—Radial load on rim.

This case is shown in fig. 3 where a radial load P is applied between the (N−1)th and Nth arms at a point defined by the angle ϕ measured from the Nth arm.

Fig. 3.



The conditions for static equilibrium of the wheel now become

$$(H_1 \cos 2\theta + H_2 \cos 4\theta \dots H_N) + (T_1 \sin 2\theta + T_2 \sin 4\theta \dots T_{N-1} \sin 2(N-1)\theta) = P \sin \phi \quad . \quad . \quad . \quad (19)$$

$$-(H_1 \sin 2\theta + H_2 \sin 4\theta \dots H_{N-1} \sin 2(N-1)\theta) + (T_1 \cos 2\theta + T_2 \cos 4\theta \dots T_N) = -P \cos \phi, \quad . \quad . \quad (20)$$

$$R_0(H_1 + H_2 \dots H_N) + (M_1 + M_2 \dots M_N) = 0. \quad . \quad . \quad . \quad (21)$$

The compressive tangential force in the rim, and the bending moment at a point α from the Nth arm when

$\alpha < (2\pi - \phi)$ will be the same as for Case I. and formulæ (5) and (6) are applicable.

When $\alpha > (2\pi - \phi)$ the extra terms to be added to these equations are $P \sin(\alpha + \phi)$ and $-PR \sin(\alpha + \phi)$ respectively.

The equations derived from $\frac{\partial U}{\partial M_0} = 0$, $\frac{\partial U}{\partial H_0} = 0$, and $\frac{\partial U}{\partial V_0} = 0$ are, except for the terms involving P, of the same form as in the case of a tangential load and are given in (22), (23), and (24).

$$\begin{aligned} &2\pi(M_0 + RH_0) - R(T_1 + T_2 \dots T_N) \\ &\quad + 2\theta\{R_0(H_1 + 2H_2 + 3H_3 \dots NH_N) + (M_1 + 2M_2 \dots NM_N)\} \\ &\quad - PR = 0. \end{aligned} \tag{22}$$

$$\begin{aligned} &(A+B)\Big[\pi RH_0 + \frac{R}{2}\{H_1 \sin 2\theta + H_2 \sin 4\theta \dots H_{N-1} \sin 2(N-1)\theta\} \\ &\quad + R\theta\{(H_1 \cos 2\theta + 2H_2 \cos 4\theta \dots NH_N) \\ &\quad + (T_1 \sin 2\theta + 2T_2 \sin 4\theta \dots (N-1)T_{N-1} \sin 2(N-1)\theta)\} \\ &\quad - \frac{PR}{2}(2\pi - \phi)\sin\phi\Big] \\ &- A\Big[\{M_1 \sin 2\theta + M_2 \sin 4\theta \dots M_{N-1} \sin 2(N-1)\theta\} \\ &\quad + R_0\{H_1 \sin 2\theta + H_2 \sin 4\theta \dots H_{N-1} \sin 2(N-1)\theta\}\Big] = 0. \end{aligned} \tag{23}$$

$$\begin{aligned} &(A+B)\Big[\pi RV_0 + \frac{R}{2}\{T_1 \sin 2\theta + T_2 \sin 4\theta \dots T_{N-1} \sin 2(N-1)\theta\} \\ &\quad + R\theta\{(H_1 \sin 2\theta + 2H_2 \sin 4\theta \dots (N-1)H_{N-1} \sin 2(N-1)\theta) \\ &\quad - (T_1 \cos 2\theta + 2T_2 \cos 4\theta \dots NT_N)\} \\ &\quad + \frac{PR}{2}\{\sin\phi + (2\pi - \phi)\cos\phi\}\Big] \\ &+ A\Big[\{M_1 \cos 2\theta + M_2 \cos 4\theta \dots M_N\} \\ &\quad + R_0\{H_1 \cos 2\theta + H_2 \cos 4\theta \dots H_N\}\Big] = 0. \end{aligned} \tag{24}$$

The remainder of the work follows closely the treatment described in the first case and the results given in eqs. (13), (14), (15), (16), (17), and (18) can be used for the present type of loading.

Having found M_1, H_1, T_1, etc. the values must be substituted in equations (19), (20), and (21), and (22), (23), and (24) to solve for M^N, H_N, T_N and M_0, H_0, and V_0.

The two special cases considered in the previous type of loading will now be examined.

Wheel in which the rim is rigid.

The equations for M_r, H_r, and T_r are as in the case of a tangential load, and from the equations of static equilibrium we find

$$H_N = \quad P \sin\phi + \alpha^n \left\{ \frac{3}{L} + \frac{3R_0N}{L^2} + \frac{CR_0N}{4L^2D} \right\}$$

$$+ \beta_n \left\{ \frac{N-2}{L} + \frac{CN}{12LD} \right\},$$

$$T_N = -P\cos\phi - T_N \left\{ \frac{6DN}{C} + \frac{N-2}{2} \right\},$$

$$M_N = -PR_0 \sin\phi - \alpha_n \left\{ \frac{R_0^2N}{L^2}\left(9 + \frac{C}{4D}\right) + \frac{6R_0N}{L} + 2(N-1) \right\},$$

$$-\beta_n \left\{ \frac{R_0N}{L}\left(1 + \frac{C}{12D}\right) + 1 \right\}.$$

From these results

$$\alpha_n = \quad 0,$$

$$\beta_n = -\frac{3P}{N}\left\{ \frac{L\sin\phi}{3 + \frac{C}{4D}} \right\},$$

$$T_N = -\frac{2P\cos\phi}{N\left(1 + \frac{12D}{C}\right)}.$$

If $\frac{C}{D}$ is very large it will be found that

$$H_{\text{max.}} = \frac{24PD}{CN},$$

$$M_{\text{max.}} = \frac{12PDL}{CN}.$$

These occur in the arm which is parallel to the load but are negligible since $\frac{C}{D}$ is large.

The maximum value of T occurs when the load acts at the end of one arm and its value in that arm is $-\frac{2P}{N}$, *i. e.* it is compressive.

The value of T_r becomes

$$T_r = -\frac{2P}{N}(\cos \overline{2r\theta+\phi}),$$

giving the axial load in any arm.

Wheel in which the arms are rigid.

As in the first case,

$$T_1 = T_2 = \dots T_{N-2} = 0,$$
$$H_1 = H_2 = \dots H_{N-2} = 0,$$
$$M_1 = M_2 = \dots M_{N-2} = 0.$$

From the equations for static equilibrium we have

$$H_N = \quad P\sin\phi - H_{N-1}\cos 2\theta + T_{N-1}\sin 2\theta,$$
$$T_N = -P\cos\phi - T_{N-1}\cos 2\theta - H_{N-1}\sin 2\theta,$$
$$M_N = -M_{N-1} - R_0\{H_{N-1}(1-\cos 2\theta) + T_{N-1}\sin 2\theta + P\sin\phi\}.$$

And since M_0, H_0, and V_0 are all zero, we have from equations (22), (23), and (24):

$$H_{N-1}\left(\frac{R}{2}\sin 2\theta + R\theta\cos 2\theta - R_0\sin 2\theta\right)$$
$$-T_{N-1}(R\theta\sin 2\theta) - M_{N-1}\sin 2\theta - \frac{PR}{2}\phi\sin\phi = 0,$$

$$H_{N-1}\{R_0(1-\cos 2\theta) - R\theta\sin 2\theta\}$$
$$+T_{N-1}\left\{\frac{R}{2}\sin 2\theta - R\theta\cos 2\theta\right\} + M_{N-1}(1-\cos 2\theta)$$
$$-\frac{PR}{2}\{\sin\phi + (4\pi-\phi)\cos\phi\} = 0,$$

$$H_{N-1}\{2\theta R_0 - R\sin 2\theta\} + T_{N-1}\{R(1-\cos 2\theta)\}$$
$$+2\theta M_{N-1} - PR\cos\phi = 0.$$

These, again, in any special case, can be readily solved, although the expressions for the general solution are somewhat cumbersome.

Example of a wheel with two spokes.

As an example of the results obtained by the foregoing method of analysis a wheel with two spokes was investigated. The particulars assumed in making the calculations were as follows :

$$R_0 = 0{\cdot}25\,R,$$

$$\frac{A}{C} = 1,$$

$$\frac{C}{D} = 1080.$$

B was negligible compared with A.

These values give a rim of the same order of rigidity as the arms.

The load P was applied tangentially to the rim and the resultant actions were found for the two cases $\phi=0$ and $\phi=\pi$.

By taking these two cases a check on the accuracy of the method was provided since the values of T_1, M_1, and H_1 in one case should become those of T_2, M_2, and H_2 in the other case, and *vice versa*.

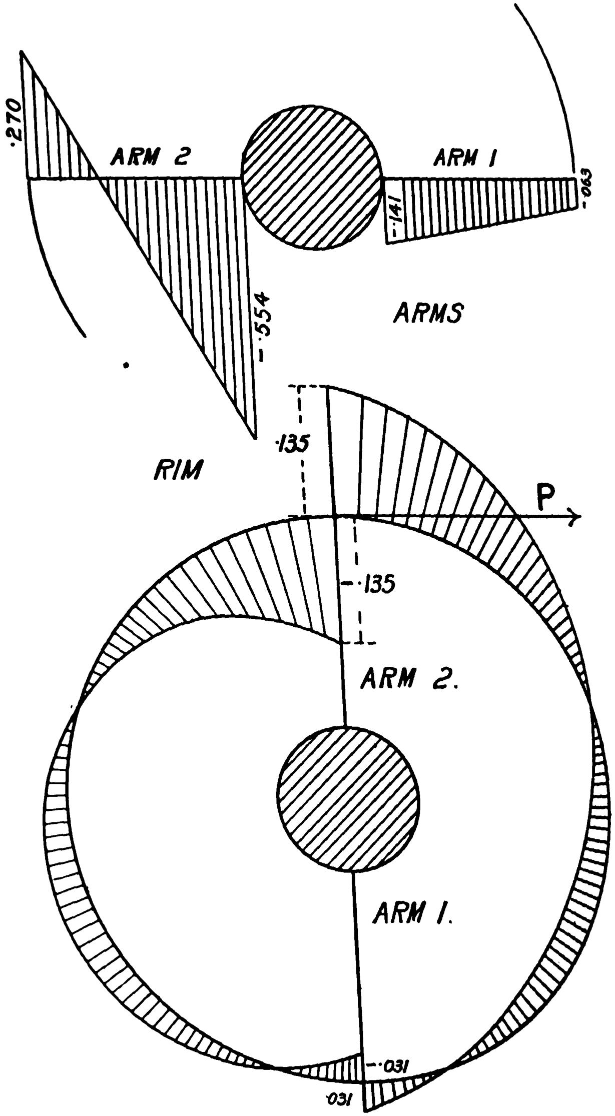
Further, the values of M_0, H_0, and V_0 for $\phi=\pi$ can be deduced from the results of the analysis for $\phi=0$ by calculating the actions in the rim just past the first arm.

The results are given in the following table :—

ϕ.	$\frac{M_0}{PR}$.	$\frac{H_0}{P}$.	$\frac{V_0}{P}$.	$\frac{T_1}{P}$.	$\frac{T_2}{P}$.	$\frac{H_1}{P}$.	$\frac{H_2}{P}$.	$\frac{M_1}{PR}$.	$\frac{M_2}{PR}$.
0	·135	−·052	·106	0	0	·104	1·104	·142	·554
π	−·030	−·055	−·108	0	0	1·101	·101	·554	·141

The deduced values of M_0/PR, H_0/P, and V_0/P are −·031, −·052, and −·106 respectively. Within the limits of accuracy adopted in calculation therefore the agreement of these and of the other quantities may be considered good.

Fig. 4.



BENDING MOMENTS IN 2 ARMED WHEEL
Ordinates give M/PR

The bending moment diagrams for the rim and arms have been plotted in fig. 4 for the case $\phi = 0$.

CONCLUSION.

The analysis of the problem given in this paper has been kept in as general a form as possible so that a complete solution might be presented. This attempt at generality has made the results appear to be complex, and although the arithmetical work required in a particular case is straightforward in character it must be done with considerable accuracy since small differences of large numbers are involved.

From the standpoint of design it is generally sufficient to obtain results of an approximate nature, and it is hoped at a later date to develop the results of this analysis, by the introduction of simplifying assumptions, to a form which will make them more readily available for application to design.

CXIX. *Critical Potentials and X-ray Term Values.*

By ANN CATHERINE DAVIES, *D.Sc., and* Prof. FRANK HORTON, *Sc.D., F.R.S.*[*]

THE critical potentials for the production of soft X-rays from solids have been investigated during the course of the last few years by several investigators[†]. The method employed in such investigations consists essentially in bombarding a solid target of the element under test by electrons from a hot filament, the energy of these electrons being varied by varying the voltage used to accelerate them. The radiation emitted as the result of the bombardment is measured by its photoelectric action on a suitably placed electrode, and the ratio of the photoelectric current per unit bombarding current for any target is plotted against the voltage corresponding to the energy of the electrons bombarding the target, obtained by adding a correction for various factors to the value of the applied accelerating potential difference. The voltages at which discontinuities in the resulting curves occur are taken as critical points indicating stages in the excitation of the targets, and therefore as being related to the different "shells" of electrons in the atoms of the targets, and to their X-ray levels.

---

[*] Communicated by the Authors.

[†] O. W. Richardson and C. B. Bazzoni, Phil. Mag. xlii. p. 1015 (1921).
O. W. Richardson and F. C. Chalklin, Proc. Roy. Soc. A, cx. p. 247 (1926).
E. H. Kurth, Phys. Rev. xviii. p. 461 (1921).
F. L. Mohler and P. D. Foote, Sci. Papers, Bur. of Standards, No. 425 (1922).
J. Holtsmark, *Phys. Zeit.* xxiii. p. 232 (1922), and *Phys. Zeit.* xxiv. p. 225 (1923).
J. C. McLennan and M. L. Clark, Proc. Roy. Soc. A, cii. p. 389 (1923).
U. Andrewes, A. C. Davies and F. Horton, Phil. Mag. xlvi. p. 721 (1923); Proc. Roy. Soc. A, cx. p. 64 (1926).
C. B. Bazzoni and C. T. Chu, Journal Franklin Institute, 197. p. 183 (1924).
C. T. Chu, Journal Franklin Institute, 200. p. 615 (1925).
G. K. Rollefson, Phys. Rev. xxiii. p. 35 (1924), & xxv. p. 740 (1925).
J. C. Boyce, Phys. Rev. xxiii. p. 575 (1924).
M. Levi, Trans. R. S. Canada, xviii. p. 159 (1924).
C. H. Thomas, Phys. Rev. xxv. p. 322 (1925), & xxvi. p. 739 (1925).

The outstanding feature of the curves obtained in such investigations is the large number of critical points which they show, and in consequence of this, the interpretation of the results presents considerable difficulty. There appear to be many more potentials which represent critical stages in the production of radiation than can be accounted for by the ionization of the successive shells of the bombarded atoms. Moreover, where an element has been examined by several investigators, the results obtained are not satisfactorily concordant either as regards the number of critical points found within any given voltage range, or as regards the actual values of critical points. Dr. Andrewes, working with the authors, has examined a series of seven elements of consecutive atomic numbers, Cr (24), Mn (25), Fe (26), Co (27), Ni (28), Cu (29), Zn (30), over a voltage range extending from 0–230. Some of these elements have been examined by other investigators, some of whom (Thomas, Rollefson, Richardson and Chalklin) have recorded many more critical points in their curves than were obtained by Dr. Andrewes and the authors. The fact that different investigations yield very different results as regards number of critical points indicated, suggests at once that in the cases where only a few indications are obtained only the more fundamental types of atomic disturbances are being effected, and that in the other cases the experimental conditions are such as to facilitate a greater variety of atomic disturbances. The intensity of the bombarding electron stream is a factor which might be expected to influence the variety of disturbances possible, very considerably, and in the experiments of Thomas and of Rollefson the intensity of the bombarding electron stream was certainly considerably greater than in the experiments of Dr. Andrewes and the writers.

In the later of the two papers previously referred to, the authors have discussed the question of a possible explanation of the several points they obtained for each element, and the correlation between these points and X-ray levels. They have shown that for all the elements they investigated, critical points falling within the range of those found must be associated with the M shell of electrons. Employing X-ray data for the heavier elements, and for the light elements in so far as data were available, and extrapolating in the case of elements where X-ray measurements had not been made, reasons were given for selecting particular critical points for each element as corresponding to the M_{I} and $M_{II, III}$ absorption limits of those elements, an absorption edge being taken to correspond to a displacement of an electron from its usual shell to the first possible unoccupied (or virtual) orbit. It was argued that there might be critical points at voltages somewhat higher than those corresponding to absorption edges, at which electrons from the shells concerned might be removed to successively more distant virtual orbits until actual ionization of the shells occurred.

For convenience of reference the values of the critical potentials found in the experiments referred to are given below in tabular form. The figures in the different vertical columns *a*, *b*, *c*, etc. indicate what the authors took to be corresponding critical points for the different elements in interpreting their results.

TABLE I.

Critical potentials (volts).

	g.	*f.*	*e.*	*d.*	*c.*	*b.*	*a.*
Cr (24).........	...	60	70	...	143	160	173
Mn (25)	...	68	83	100	152	174	184
Fe (26).........	47	73	90	106	166	181	...
Co (27).........	...	..	94	113	171	191	...
Ni (28).........	...	...	104	...	178	196	...
Cu (29)	...	...	112	...	193	206	...
Zn (30).........	...	...	119	...	200	214	...

In an extension of the investigation, at present in progress, using a modification in the method of measurement of the radiation current, indications of critical potentials in the lower region of the curves, corresponding to the *g* and *f* points for iron, have been obtained with the other targets. As the investigation is not yet completed, and as in the light of these newer indications some modifications may be necessary in the correlation of the various critical points in different elements, the additional values are not included in Table I.

By plotting the $\sqrt{(\nu/R)}$ values of the voltages given in the table against the atomic numbers of the elements, and by constructing the $\sqrt{(\nu/R)}$ against atomic number curves for various X-ray levels, and differences of X-ray levels, from X-ray line and absorption edge measurements, the value in the *g* column was shown to be that most nearly corresponding to a displacement to the periphery of the atom, of an electron from the group associated with the $M_{II, III}$ level, while the values in column *d* were shown to be those most nearly corresponding to similar transitions from the electron group associated with the level M_I. In the case of the $M_{II, III}$ level, the correlation could be made directly as the requisite X-ray line measurements were available for the elements in question. In the case of the M_I level, the correlation had to be made by extrapolation from X-ray data extending only down to atomic number 37. From the sequence of the points *g*, *f*, and *e*, and of the points *d*, *c*, and *b*, for iron, and by analogy for the other elements, it was suggested that the *g*, *f*, and *e* values were connected with displacements of an electron from the group associated with $M_{II, III}$ to different final positions, and the points *d*, *c*, *b*, and *a* with displacements to various final positions of an electron from the group associated with M_I.

Some precision X-ray measurements of certain L lines* for some of the elements investigated by Dr. Andrewes and the authors, published since the date of their paper, make it now possible to calculate entirely from X-ray data the values of $M_I - N_{II, III}$ for these elements. These quantities cannot differ very much from the values of the energy of the first possible transition from the electron shells associated with M_I in the different atoms, and they show that the critical potentials given in column *e* of the table, rather than those in column *d*, are the ones which should be connected with such displacements, in spite of the fact that the *d* points rather than the *e* points appear to be most nearly in line with the corresponding values for heavier elements when extrapolating.

In a recent paper † Stoner has given a discussion of the significance of measurements of critical radiation potentials, by the method outlined, and he directs attention to the point that the extent of the voltage differences between the various critical stages which the authors associated with displacements of an electron from a particular shell to different final positions, is much larger than could be expected for such displacements in a neutral atom. It seems to be suggested in the paper referred to that if the principal and azimuthal quantum numbers of the deepest level to which an electron from an inner shell might be removed, were known, the exact extent of the voltage difference between the extreme critical potentials for different displacements of an electron from a particular shell in the neutral atom, could be calculated from the terms of the optical spectrum of that element. Though not themselves holding this view, the authors agree with Stoner in being of the opinion that the ranges of the different points associated in their paper with different displacements from particular shells, are too wide to be attributable to such displacements in neutral atoms, *i. e.* the difference between the critical points is too large for them to be identified with the "fine structure" of an X-ray absorption stage, predicted by Kossel.

---

* R. Thoræus, Phil. Mag. ser. 7, i. p. 312 (1926).

† E. C. Stoner, Phil. Mag. ser. 7, ii. p. 97 (1926).

The following considerations bear upon the question of the actual magnitude of the "fine structure" of an absorption stage. If an electron from the K shell of an atom is removed to the periphery of the atom, then, neglecting for the moment the question of selection principle rules in regard to transitions, one might expect that some indication of the new constitution of the outer part of the atom might be obtained by reference to the atomic structure of the element next higher in the order of atomic number. As regards the firmness of binding of electrons in the exterior parts of the atom, the effect of removing an electron from the K shell is practically the same as the effect of increasing the nuclear charge by one unit. Hence the electron removed from the K shell will occupy the most firmly bound position in the resulting system when it and the already existing valence electrons form a system similar to the system of outer electrons in the next higher element. In such a case the energy required to transfer the K electron from this position, and to detach it completely from the atom, would be practically the same as the energy corresponding to the ionizing potential of the next higher element (possibly very slightly less). Hence the "fine structure" of the K absorption edge attributable to displacements to virtual orbits in the neutral atom could not correspond to a voltage difference exceeding the ionizing potential of the next higher element.

That the screening action of electrons in other shells falls more and more short of perfect as we deal with shells successively more distant from the nucleus in any atom is well established, and Turner has shown in a recent paper [*] that the non-diagram X-ray lines related to K_{α_1}, measured by Hjalmar [†] for certain light elements, admit of interpretation on the basis of Wentzel's theory of multiple ionization of the K and L shells in a way which, if the interpretation be correct, provides definite evidence that the removal of an L electron produces a smaller increase in the amount of energy required for the subsequent removal of an M electron than is produced by the removal of a K electron. It therefore seems reasonable to assume that the removal of an M electron increases the energy required for the subsequent removal of an N electron by a still smaller amount. Hence, if the M electron were removed merely to the nearest possible virtual orbit, the energy required subsequently to remove it completely from the atom would be less than would be required for the corresponding process in the case of an electron from the K shell. Therefore in a neutral atom the "fine structure" of an M absorption stage must correspond to a range of voltage quite definitely less than the ionizing potential of the next higher element.

If we attempt to predict from the selection rule governing changes of azimuthal quantum number, to which virtual orbits an electron ejected from any particular sub-group of electrons may go, we have to bear in mind not only the recent work of Heisenberg [‡] and of Hund [§] in regard to the term character of incomplete electron configurations, but also that the azimuthal quantum numbers ordinarily assigned to the various levels characterize the singly ionized shells, whereas in the initial stage of the transitions contemplated the shell is complete.

These considerations show the difficulties which would have to be overcome in any attempt to estimate from optical terms, either of the neutral or the ionized atom, exactly what "fine structure" to expect. Nevertheless, as has already been shown, we can, in cases where the optical data are available, or where the ionization potentials have been measured, obtain an upper limit which the extent of the "fine structure" cannot exceed in a system of any definite degree of ionization.

Stoner has suggested that some of the many critical points found in experiments of the type under consideration are accounted for by impacts which disturb electrons from the inner shells in atoms already singly, doubly, or trebly ionized in an optical sense. A difficulty in the way of accepting this explanation is that one would expect to be able to classify the points corresponding to any particular degree of opitical ionization according to the intensities of the effects produced at the critical stages, because the proportions of atoms in the bombarded surface existing at any instant in the various degrees of ionization would be likely to be very different. In the experiments of Dr. Andrewes and the authors it did not appear that a classification of points on such a basis could be made. It seems to the writers more probable that the electron impacting on any given atom with energy sufficient for the purpose, might itself produce a certain degree of optical ionization in addition to disturbing an electron from an inner level of the atom. Such occurrences would give a wider range of voltages to be associated with any given degree of optical ionization than would be given by the bombardment of already ionized atoms, and they would not necessarily give bends in the curves of very different orders of magnitude according to the degree of ionization, because the greater multiplicity of the disturbing effects produced on the atom would result in the emission of more radiation quanta in the process of reorganization of the atom, the higher the degree of optical ionization produced, and this would tend to compensate for the possible less frequent occurrence of the more complicated disturbances.

---

[*] L. A. Turner, Phys. Rev. xxvi. p. 143 (1925).

[†] E. Hjalmar, *Zeit. f. Phys.* i. p. 439 (1920).

[‡] W. Heisenberg, *Zeits. f. Phys.* xxxii. p. 841 (1925).

[§] F. Hund, *Zeits. f. Phys.* xxxiii. p. 345 (1925).

Instances of the detection of critical potentials corresponding to the simultaneous removal of more than one electron from an atom are well known, *e. g.*, the double ionization potential of helium, 78·8 volts. Other instances of the occurrence of multiple effects at single impacts are to be found in the results of investigations of the potentials necessary for the production of spark lines of the spectra of the rare gases.

To quote a definite instance for the upper limit of the order of magnitude of the difference of the critical potentials possibly associated with the disturbance of any particular electron in an atom in a given state of optical ionization :— The ionizing potential of Mn (25) is 7·4 volts*. Therefore if we disturbed a K electron in Cr (24), taking it first to the lowest possible virtual orbit, and then removing it completely, the final process would not require more than 7·4 volts. Similarly if we disturbed in the same two stages a K electron in a chromium atom which had already lost its outermost electron, the final process would not require more energy than that corresponding to the ionization potential of singly ionized manganese, *i. e.*, 14·5 ± 0·4 volts *. Since to remove the most loosely attached electron from a normal chromium atom requires 6·8 volts, the potential difference required to give the energy necessary to remove at one electron impact the outermost electron and an electron from the K shell would differ very little from (6·8 + V + 14·5 ± 0·4) volts, where V denotes the voltage required for the removal of the electron from the K shell to the lowest virtual orbit. As Stoner has pointed out, the energy necessary for such a transition will vary very little with the removal of outer electrons. Hence (6·8 + 14·5 ± 0·4) volts is the maximum difference of the critical potentials which might be associated with transitions of a K electron in a chromium atom without assuming a higher state of optical ionization than the first. The corresponding difference for transitions of an M electron in a chromium atom would, of course, be likely to be less than this, but this may be taken as an upper limit. If we assume that the upper limit for the corresponding differences in the other elements is of the same order of magnitude, we see that the *d* points might conceivably be connected with the *e* points in this way, *i. e.*, that the *e* points correspond to the removal of an electron from a group associated with M_{I} to the periphery of a neutral atom, while the *d* points correspond to the complete removal of such an electron simultaneously with the removal of one of the most loosely bound electrons.

---

* M. A. Catalan, Phil. Trans. Roy. Soc. A, ccxxiii. p. 127 (1923).

Whether the *f* points correspond to the complete removal of an electron from the group associated with $M_{II, III}$ simultaneously with the removal of an optical electron is uncertain, since the values for the other elements corresponding to the *g* value for iron, were not indicated in the curves. In the case of iron the difference between the two lowest points is 26 volts, whereas the difference between the *d* and *e* points is only 16 volts. Such a large discrepancy as this makes it doubtful whether we can justifiably assume *g* and *f* to be related similarly to the points *e* and *d*. Possibly the *f* points correspond to the removal of an $M_{II, III}$ electron simultaneously with the removal of more than one optical electron, though in this case it is difficult to see why the curves do not give indications of the removal of an $M_{II, III}$ electron simultaneously with the removal of *one* optical electron.

Considering the *a*, *b*, and *c* points, it does not seem that they can be explained in any simple way on the basis of higher stages of optical ionization. Stoner has suggested that they are due to multiple impacts, *i. e.* an electron hitting first one atom and disturbing it, and then disturbing another atom with the energy retained after the first collision. In regard to this suggestion, the objection might again be urged that the indications of such occurrences would be expected to be very much less marked than the indications of events involving only single impacts.

---

* D. R. Hartree, 'Nature,' cxvi. p. 356 (1925).

The order of magnitude of the *a*, *b*, and *c* values in relation to the lower values is such that they might be due to multiple disturbance of the M shell by single electron impacts, either the disturbance of two electrons from the sub-group associated with $M_{II, III}$ or the disturbance of one from each of the sub-groups associated with $M_{II, III}$ and M_I, or even possibly the disturbance of two electrons from among those associated with M_I. Evidence of the production of atoms multiply disturbed in their X-ray levels is to be found in the non-diagram X-ray lines which Wentzel has shown can be satisfactorily explained on the basis of states of multiple ionization of the inner region of the atom. In a recent letter to 'Nature,' Robinson[*] records the production of different lines in the magnetic spectrum of the electrons emitted from a target exposed to X-rays when internal absorption by the atoms of the target, of the K radiations excited in them by absorption of the primary radiation, takes place. These lines he attributes to the ejection of L electrons from atoms in which the L shell is already ionized. Robinson states that he has so far obtained no evidence of the production of multiple ionization by a single X-ray quantum, but it does not follow that the effects obtainable by electron bombardment would be limited to those correspondng to the effects produced by X-ray absorption, so that the lack of evidence of multiple X-ray ionization by a single quantum does not invalidate the suggestion that such a process may occur as the result of electron impacts[†].

If multiple ionization of an atom can take place as the result of absorption of a single quantum, then it is possible that some of the critical points obtained by various investigators are due to the occurrence of this effect in the electrode exposed to the radiation emitted by the target. As the energy of the bombarding electrons increases, the quality of the general X-radiation varies, and it is possible that at certain values of the accelerating potential the general radiation is able to eject two or more electrons from the illuminated electrode by the absorption of individual quanta. Such occurrences would be expected to cause the appearance of discontinuities in the radiation curves. Effects of this kind might be described as discontinuities in the photoelectric current due to the general radiation, as distinct from discontinuities in the general radiation itself, suggested by Richardson and Chalklin. It would appear, however, that in experiments involving the use of several targets in turn, it should be possible to distinguish between discontinuities due to this cause and those characteristic of the target under test, because those produced by changes in the action of the general radiation on the electrode exposed to it should appear at the same voltages in the curves for all the targets. The absence of discontinuities common to all the targets may be taken as evidence of the non-occurrence of effects of the type discussed, and also, in conjunction with the many critical points which have been obtained, as indicating that many more types of atomic disturbance can be produced by electron impacts at suitable voltages, than by exposure to radiations of corresponding frequencies.

---

[*] H. Robinson, 'Nature,' cxviii. p. 224 (1926).

[†] The experiments of Siegbahn and Larsson on the voltages necessary for the excitation of the satellites of the L_α line for molybdenum seem to provide evidence that the simultaneous disturbance of two electrons from X-ray levels by a single electron impact does occur (Sci. Abs. 577 1925).

This raises an interesting point in connexion with the interpretation of results obtained in the "magnetic spectrum" method of investigation of X-ray levels, and the possibilities of the method in regard to the unravelling of the more complicated phenomena. In the case of multiple ionization by a single X-ray quantum, the determination of the amount of energy actually involved in the ejection of each electron might be a matter of very considerable difficulty, for the manner of distribution of the excess energy of the quantum above that required for the actual removal of the two electrons would not be known, and it might be very difficult to recognize which pairs of lines in the magnetic spectrum should be considered together. In the case of internal absorption of one of the characteristic wave-lengths by an atom already ionized in one of its inner shells, the determination of the energy value of the level in such an atom would follow directly from the difference between the energy of the characteristic radiation absorbed and that of the electrons giving the line in the magnetic spectrum. Hence, if we take the view that multiple ionization by absorption of single quanta does not occur *, the results of investigations

---

* D. Coster and J. H. van der Tuuk in a recent paper in the *Zeits. f. Phys.* (xxxvii. p. 367, 1926) have concluded that transferences of two or more electrons simultaneously appear to play no part in X-ray absorption spectra.

of energy level values by determining, by the method of magnetic bending, the energies of the electrons emitted from a target of the material irradiated by X-rays of known frequency, may be expected to be more easily interpreted, and to yield more direct values than the results of investigations of critical potentials for the production of radiation, though up to the present time the former method does not appear to have been developed for use in connexion with the accurate determination of the levels of relatively low energy value.

The very factor which puts the critical potential method at a disadvantage as regards the determination of the normal X-ray level values of atoms—namely the greater variety of atomic disturbances produced by electron impact—constitutes a strong reason for the further development of that method, in that it promises a means of obtaining information unobtainable by the other method, when once ways of facilitating the interpretation of the results are devised. A possible method whereby the identification of the nature of the atomic disturbances produced at the various critical stages might be achieved, would appear to be by combining with the location of critical points a determination of the distribution of velocities among the photoelectrons emitted by the radiation produced just above and just below each one.

CXX. *Dimensional Analysis Again.*

By P. W. BRIDGMAN [*].

THE subject of dimensional analysis has been so much discussed in the pages of the Philosophical Magazine in the last few years that one would like to see it die a natural death, were it not that in the last two communications [†] things have taken such a turn that an unchallenged acceptance of the views there presented may easily affect the use which the physicist makes of this analysis.

My position on this general subject has already been expounded in considerable length and detail in my book 'Dimensional Analysis,' Yale University Press, 1922. This book was written primarily because there was nowhere any previous attempt to give a systematic examination of the arguments on which the dimensional method rests, nor to show how it may be applied in many of the cases of practice, although the dimensional method was used to a greater or less degree by nearly every physicist, and there were incomplete and incidental references to the theory in a great many places. Now in these previous incomplete references were contained many misconceptions and fallacies; it was the first task of the book to show what these fallacies were. Among these fallacies was the idea that an equation expressing a connexion between physical things must be dimensionally homogeneous. I then showed that, in spite of the unsatisfactory form in which the dimensional argument had been often stated, it was possible to put it on a thoroughly sound basis, and apply the method with confidence to the solution of many important problems. I particularly stressed the point that the method, when properly understood, has nothing esoteric about it, that it gives no information which we did not have already in a less available form, and that therefore an adequate physical grasp of each individual problem is necessary. No refinement of mathematical argument will give correct results if our physical grasp of the broad features of the problem is inadequate. Just here is the feature in which my treatment differed most from those preceding; I emphasized that the broad physical grasp necessary to an application of the method finds expression in a knowledge of the *general character* of the equations which govern the motion of the system. Only in this way could the puzzling matter of dimensional constants be satisfactorily treated. Thus if the problem is one involving fluid motion, as in discussing airplane problems, the governing equations are those of hydrodynamics, into which no dimensional constants enter, so that no such constant enters the final result; but if the problem is one of electrodynamics, the field equations of electrodynamics govern, which do contain a dimensional constant (velocity of light, or ratio of units), and the dimensional constant may be expected in the final result.

---

[*] Communicated by the Author.

[†] Mrs. T. Ehrenfest-Afanassjewa, Phil. Mag. [7] i. pp. 257-272 (1926); Norman Campbell, Phil. Mag. [7] i. pp. 1145-1151 (1926).

For the method, purged from many previous fallacies and made (comparatively) rigorous, I used the name "Dimensional Analysis." Now it is gratifying that the name has apparently been accepted, as shown by the titles of recent papers, but, unfortunately, not in the sense in which I used it, but with a more or less indefinite blend of many former misconceptions. Thus Mrs. Ehrenfest-Afanassjewa in particular, although generously attributing the name to me, ascribes to the "dimensional analysist" a miscellaneous assortment of errors, which even I, in my enthusiasm in my book for putting the worst light on previous misconceptions, would hardly have ventured to attach to any individual. Thus she begins by committing the dimensional analysist to the thesis that all equations expressing physical relations are dimensionally homogeneous, which is supposed to be equivalent to the statement that dimensional constants cannot occur. She then allows him to talk the most meaningless nonsense about other possible universes in which the gravitational constant might be different from ours, and she ends by making him so blind in his resolution to use only a pure dimensional method that he forgets that he knows that the gravitational attraction of the earth varies inversely as the square of the distance, and so is unable to find how the period of a pendulum varies with the distance from the earth's centre.

Of course Mrs. Ehrenfest-Afanassjewa has no trouble in making merry with her poor analysist. Now comes the important point for the physicist. Because of these difficulties, she would have us abandon the dimensional method altogether, and substitute for it another, which she calls the theory of similitudes, much more mathematical in character, and much more difficult for the physicist to apply, as one may see on reading her treatment of the simple pendulum problem. There are many formal resemblances between the methods, as she points out, but that they are not the same is shown by the fact that they do not always give the same solutions. The method of similitudes resembles that of dimensional analysis as expounded in my book in that the important role of the fundamental equations governing the motion of the system is recognized, but there is a vital difference in that her method demands a knowledge of the equations in *detail*, whereas the dimensional method needs to know only the general character of the equations. It is well known that the dimensional method has its most important practical application in such complicated problems as that of the airplane, where it is hopeless to attempt to write the equations in detail. I do not see how Mrs. Ehrenfest-Afanassjewa's method can be applied to this problem at all. On the other hand, dimensional analysis, in the sense expounded in my book, can certainly solve all the problems which she gives to show the limitations of dimensional analysis, and she will further find in my book an explanation, on purely dimensional grounds, of the questions raised in the correspondence between Lord Rayleigh and Riabouchinsky which she discusses in her paper from the standpoint of her theory.

The main purpose of this note is then to dispute the conclusion that might be drawn from an unchallenged acceptance of Mrs. Ehrenfest-Afanassjewa's paper. I believe that the dimensional method *can* be made rigorous, that it is *not* necessary to replace it by the mathematical method of similitudes which she offers, that the dimensional method is much easier for the physicist to apply, and in many important practical cases is more powerful.

Opposed to Mrs. Ehrenfest-Afanassjewa is Norman Campbell, who will have none of her method of similitude, but prefers that of dimensions. However, I cannot agree with Campbell, as it seems to me that his argument is put on an incorrect basis. It is certainly not necessary to assume that physically similar systems are possible in order to apply the dimensional method. For example, the deduction of the relation between the mass of an electron, its charge, radius, and velocity of light (dimensional constant of the electrodynamic equations) does not involve the assumption at all that more than one kind of electron is physically possible. Neither is it necessary in deducing the pendulum formula to so far analyse the situation as to recognize that "the period of the pendulum seems to be the physical sum of elementary periods, during each of which it may be supposed to move with constant acceleration." I fear that if as deep an analysis as this were necessary, few physicists would ever have the courage to attempt a dimensional analysis at all.

The Jefferson Physical Laboratory,
Harvard University, Cambridge, Mass.

CXXI. *The Atomic Structure of AgMg and AuZn.* By E. A. Owen, *M.A.*, *D.Sc.*, *and* G. D. Preston, *B.A.*, *National Physical Laboratory* *.

In a previous paper the authors gave an account of the determination of the atomic structure of the two intermetallic compounds Mg_2Si and AlSb †, which were examined by the X-ray spectrometer. The present paper is a continuation of this work and contains the data obtained and the structure deduced therefrom, of the compounds AgMg and AuZn. The former was examined both with the spectrometer and by the photographic method. A full account of the procedure with the spectrometer will be found in previous papers ‡. For the photographic method a Müller camera was employed, the material under examination being reduced to a fine powder and rotated in a beam of X-rays from a copper target.

---

* Communicated by the Authors.

† Proc. Phys. Soc. **xxxvi.** Pt. 5, p. 341 (1924).

‡ See Proc. Phys. Soc. **xxxv.** p. 101 (1923); **xxxvi.** p. 14 (1923); **xxxvi.** p. 49 (1923).

(1) *AgMg.*

The curve obtained with the ionization method is shown in fig. 1, the radiation employed being the K-series radiation of a molybdenum target. The analysis is given in Table I.

Fig. 1.

AgMg. Centred cube. Side $=3{\cdot}28$ Å. Molybdenum Radiation·

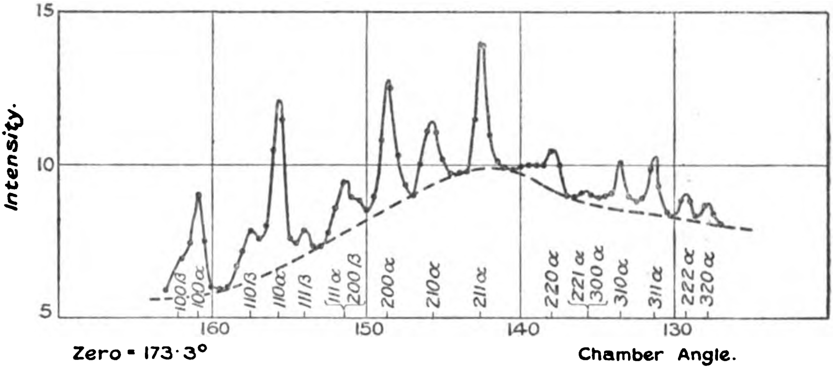


TABLE I.—AgMg plate. Molybdenum K radiation, $\lambda_a = 0{\cdot}708$ Å., $\lambda_\beta = 0{\cdot}630$ Å.

θ.	Sin θ.	Form.	λ.	*a*.	I obs.	I calc.
5°·55	0·0967	100	β	3·26 Å	8	8
6·15	0·1072	100	α	3·30	30	23
7·90	0·1374	110	β	3·24	20	19
8·80	0·1530	110	α	3·27	55	56
9·65	0·1677	111	β	3·26	8	3
10·95	0·1900	111	α	3·23	10	9
11·25	0·1951	200	β	3·23	9	4
12·30	0·2130	200	α	3·32	40	13
13·75	0·2376	210	α	3·33	10	13
		211	β	3·25	13	11
15·35	0·2647	211	α	3·28	41	31
17·70	0·3040	220	α	3·29	15	11
18·75	0·3214	221 300	α α	3·30	2	6
19·90	0·3404	310	α	3·29	12	16
21·00	0·3584	311	α	3·28	18	6
22·00	0·3746	222	α	3·27	6	5
22·70	0·3859	320 400	α β	3·31 3·27	5	5

Mean value of *a* = 3·28 Å

The lines are all accounted for by a simple cubic structure of parameter 3·28 A. The density of the material was directly determined and yielded the value 6·2 grammes per c.cm. The cube root of the molecular volume is 3·275 Å, and there are therefore one atom of silver and one of magnesium associated with the unit. The fifth column in Table I. gives the intensities of the lines as observed. In estimating the observed intensities a smooth curve (shown dotted in fig. 1) is drawn touching the lowest part of the observed curve. The heights of the peaks above this smooth curve are taken as the intensities of the different lines. The last column of Table I. gives the relative intensities of the lines calculated on the assumption that the structure is of the cæsium chloride type, *i. e.*, that the atoms are assembled on a body-centred lattice. In the computation of the intensities the expression

$$I \propto j \left(\frac{d_{hkl}}{n}\right)^{2\cdot35} . A^2$$

has been employed, n being the order of the spectrum, j the number of cooperating planes, d_{hkl} the spacing of the plane whose indices are (hkl), and $A = 59$ or 35 according as $n(h+k+l)$ is even or odd, 59 being the sum of and 35 the difference between the atomic numbers of silver (47) and magnesium (12). The agreement between observed and calculated intensities is probably as good as can be expected.

Table II.

Powdered AgMg. Copper K radiation,
$\lambda_a = 1\cdot537$ Å, $\lambda_\beta = 1\cdot389$ Å.

θ.	Sin θ.	Form.	λ.	*a*.	I.
13°·80	0·2385	100	α	3·22 Å	s
17·75	0·305	110	β	3·24	m
19·55	0·335	110	α	3·24	vs
28·00	0·4695	200	α	3·27	s
31·50	0·5525	210	α	3·29	s
35·10	0·575	211	α	3·27	vs
41·45	0·662	220	α	3·27	m
44·65	0·703	221 300	α	3·28	m
47·30	0·735	310	α	3·30	s
50·20	0·768	320	β	3·29	vvf
51·95	0·787	311	α	3·24	vvf
53·90	0·808	222	α	3·29	vvf
57·20	0·841	320	α	3·30	vf
60·45	0·870	321	α	3·30	s

Mean value of $a = 3\cdot27$ Å

Several photographs of the material were taken by means of the Müller camera. The analysis of one photograph is given in Table II. and bears out the result obtained by means of the spectrometer.

A fact which emerged during the examination of the material by the spectrometer is that when the material is examined after being etched, a spectrum is obtained which corresponds to a face-centred cubic structure of side 4·076 Å, This figure is in approximate agreement with that given by McKeehan [*] for the parameter of the silver lattice. The etch dissolves out the magnesium from the body-centred lattice, and the silver atoms recrystallize at room temperature on a face-centred lattice. A curve obtained with the spectrometer using the etched material is shown in fig. 2, and the result is analysed in Table III.

Fig. 2.

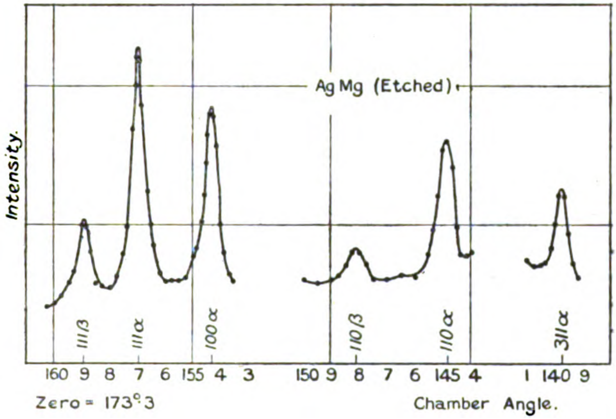


TABLE III.

Etched plate AgMg. Molybdenum K radiation,
$\lambda_\alpha = 0·708$ Å, $\lambda_\beta = 0·630$ Å.

θ.	Sin θ.	Form.	λ.	a.
7° 40′	0·1335	111	β	4·086 Å
7 40	0·1507	111	α	4·068
10 0	0·1736	200	α	4·079
12 35	0·2178	220	β	4·090
14 14	0·2459	220	α	4·070
16 47	0·2888	311	α	4·065

Mean value of a = 4·076 Å

---

[*] Phys. Rev. xx. p. 424 (1922).

(2) *AuZn.**

A small block of material of approximately the constitution AuZn was examined by the photographic method. The surface to be irradiated consisted of fairly large crystals, and was therefore rubbed on fine emery-cloth to break up the surface. The result of this treatment is to make the lines of the spectrum rather broad so that their position cannot be fixed with precision. The analysis of the photograph is given in Table IV., the observed lines being accounted for by a simple cubic structure of side 3·19 Å. The cube root of the molecular volume is 3·11, the observed density being 14·4 grammes per c.cm. As in the case of AgMg, there are therefore two atoms in the unit. The relative intensities of the lines are in accordance with a cæsium chloride structure.

TABLE IV.

Powdered AuZn. Copper radiation,

$\lambda_\alpha = 1{\cdot}537$ Å, $\lambda_\beta = 1{\cdot}389$ Å.

θ.	Sin θ.	Form.	λ.	a.	I obs.	I calc.
14°·05	0·244	100	α	3·15 Å	f	10
17·8	0·306	110	β	3·23	m	15
19·9	0·340	110	α	3·22	s	44
24·9	0·421	111	α	3·16	f	4
28·5	0·477	200	α	3·22	f	10
32·0	0·530	210	α	3·24	vf	6
36·25	0·591	211	α	3·19	s	24
43·2	0·684	220	α	3·18	f	9
61·5	0·879	320	α	3·15	f	2

Mean value of a = 3·19 A.

Summary.

The atomic structure of the two compounds AgMg and AuZn has been examined by X-ray methods. In each case the structure turns out to be of the cæsium chloride type, the parameter AgMg being 3·28 Å and that of AuZn, 3·19 A

---

* See Westgren and Phragmén, Phil. Mag. 1. p. 311 (1925).

CXXII. *On the Condenser-Telephone.*

To the Editors of the Philosophical Magazine.

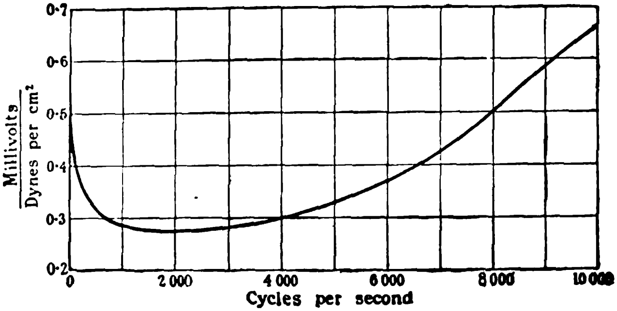
GENTLEMEN,—

IN the Phil. Mag. ser. 7, vol. ii. No. 9, September 1926 Dr. G. Green has a paper on Condenser-Telephones in which he works out their behaviour over the audio frequency band from fundamental data.

At first sight the results are somewhat perplexing, particularly to those who make use of the condenser-telephone for electro-acoustic measurement purposes.

Dr. Green shows that a small capacity condenser-transmitter such as the well-known Wente type used under the conditions he postulates would be inefficient at the lower audio frequencies. On the other hand, the Wente transmitter and most other types of condenser-transmitters under normal conditions of use have frequency-amplitude characteristics which invariably indicate a rising efficiency towards the lower end of the audio-frequency band.

The explanation lies in the circuit used by Dr. Green for his calculations. This circuit includes a transformer, and a value of inductance of the order of 0·8 henry is assumed.



Calibration of electrostatic transmitter.

Such a transformer is quite unsuitable to use as coupler between a condenser-transmitter and the grid of an amplifying valve, and, in practice, a condenser-transmitter is generally coupled to the grid of the first amplifying valve by an inductionless circuit. Under this condition the frequency-amplitude characteristic will be found to fall steadily from a maximum at low audio frequencies, and in the case of transmitters of the Wente type with stretched diaphragms having natural periods towards the upper ends of the audio-frequency band, the characteristic will again rise towards this higher frequency. As an example, the calibration of a Wente electrostatic transmitter is reproduced*.

It is thought advisable to draw attention to this apparent contradiction. Dr. Green's paper really deals with the operation of a condenser-telephone with a special and very unsuitable form of coupling so far as low capacity types of instrument are concerned.

Yours faithfully,
September 25, 1926. B. S. COHEN, M.I.E.E.

CXXIII. *Luminous Discharge in a Rapidly Alternating Field.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

MAY I be permitted to draw attention to an error which Messrs. Gill and Donaldson have made, in their criticism of my method of measurement to which I made reference in an earlier letter (Phil. Mag. vol. ii. p. 741, 1926). These authors are of the opinion that the cathode stream instrument I have employed "only measures the electric force. . . . When the discharge is passing the electric force is not uniform." May I in this connexion quote a sentence from my previous letter: "My method involves the measurement of the deflexion of an independent cathode stream in a high vacuum.". That is, the cathode stream does not pass through the discharge tube at all, but through a separate *high vacuum*, the experimental arrangement being described in detail in my paper in the *Annal. d. Physik* (vol. lxxvii. p. 287, 1925). It is obvious that in a high vacuum, where no discharge exists, the electric force between two parallel electrodes cannot be other than uniform, and therefore my cathode stream instrument measures not only the electric force, but the actual potential.

Yours faithfully,
München,
October 14, 1926.
FRITZ KIRCHNER.

---

* Physical Review, 1917, vol. x. p. 22, and 1922, vol. xix. p. 498. See also paper on Frequency Characteristics of Telephone Apparatus read before I.E.E. April 29th, 1926.

CXXIV. *On the Existence and Half-Period of Radium C.*

By A. W. Barton, *M.A., B.Sc., Trinity College, Cambridge* *.

Introductory.

SINCE Radium C emits both α and β rays it was inferred that it consists of two or more radio-active elements, and in 1909 Hahn and Meitner † obtained by recoil from it minute quantities of a new element Radium C″. The investigation was continued by Fajans ‡, who suggested the following scheme for the disintegration of radium C :—

$$\begin{tikzcd} & \text{Radium C}' \; 10^{-8}\text{ sec.?} \arrow[r] & \text{Radium D} \arrow[r] & {} \\ \text{Radium C} \arrow[ur, "\beta"] \arrow[dr, "\alpha"'] & & & \\ & \text{Radium C}'' \; 1\cdot4\text{ mins.} \arrow[r] & \text{End-Product ?} & \end{tikzcd}$$

Radium C appears to disintegrate in two different ways, 99·97 per cent. of the atoms emitting a β-particle to become Radium C′ and 0·03 per cent. emitting an α-particle to become Radium C″. Radium C′ was not isolated, its existence being only inferred ; and furthermore the value of its half-period, if it does exist, is very hypothetical as it was calculated from the range of the α-particles it emits using the Geiger-Nuttall Relation. This relation between the range of the α-particles emitted by a radio-active element and its decay constant has been shown to be only approximately true by the accurate redetermination by Geiger of the ranges of the α-particles emitted by various elements §. The consequent necessity for direct evidence on the existence and half-period of radium C′ has been rendered still more urgent by the discovery ‖ that radium C emits a few α-particles of longer range than those already known. This may mean that radium C is still more complex than indicated by the above scheme of disintegration.

Any direct method for investigating the existence of radium C′ and obtaining a rough value of its half-period depends upon obtaining an efficient β-ray recoil to separate the radium C′ from radium C. Consequently, an investigation of the conditions most favourable to this recoil was

* Communicated by Prof. Sir E. Rutherford, O.M., F.R.S.

† *Phys. Zeits.* x. p. 697 (1909).

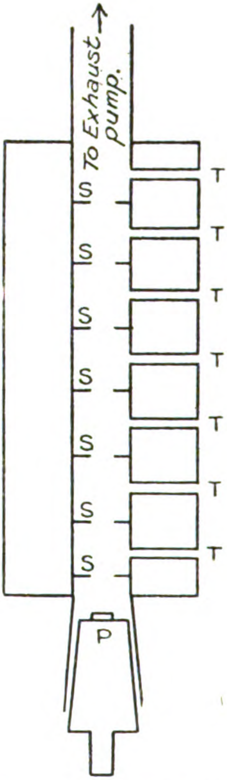
‡ *Phys. Zeits.* xii. p. 319 (1911) ; xiii. p. 699 (1912).

§ *Zeits. f. Physik*, viii. p. 45 (1921).

‖ Proc. Roy. Soc. A, cv. p. 97 (1924).

undertaken with a view to applying the results to this problem[*]. During these experiments an account of a beautiful method of isolating radium C′ and finding its half-period was published by Jacobsen[†]. He found that radium C′ exists and has a half-period of 5×10^{-5} sec., a value which does not agree with that obtained from the Geiger-Nuttall Relation. It would appear, however, that Jacobsen's experiments are open to criticism in certain respects, which will now be dealt with.

Fig. 1.



Apparatus used by Jacobsen.

His method of experiment was to project a beam of radium C′ atoms limited by the screens S from the radium C on the plate P by β-ray recoil, the whole apparatus being exhausted to a pressure of 10^{-4} mm. of mercury (fig. 1).

---

[*] Phil. Mag. i. p. 835 (1926).

[†] Phil. Mag. xlvii. p. 23 (1924).

Owing to the very short half-period of radium C′, a large proportion of the atoms disintegrate in passing down the tube, and by counting the number of α-particles per minute striking a zinc-blende screen placed opposite the tubes T in succession the half-period of radium C′ can be determined, assuming a value for the velocity of the recoil atoms. In order to be sure that the α-particles so counted are due to the disintegration of radium C′ and not to spurious effects such as scattering or "contamination," a count is taken with the pressure in the apparatus at about 5 mm. of mercury to stop the radium C′ atoms, and the number so obtained subtracted from the corresponding value with the pressure at 10^{-4} mm. There are, it would seem, three objections to this method of carrying out the experiment:—

(1) Some of the α-particles counted in the tube nearest to the plate D may be due to scattering.

(2) The method of testing that the α-particles counted are due to the disintegration of radium C′ is unsatisfactory, as an increase of pressure would effect contamination and possibly other spurious effects.

(3) An efficiency of recoil of 2 per cent. would be required to obtain the actual effects quoted in Jacobsen's paper. That this has never been previously obtained under the conditions he used constitutes the chief objection to accepting his results as final.

It seemed advisable to repeat this experiment chiefly because of the great importance of the problem itself, at the same time endeavouring to eliminate as far as possible the features criticised above in Jacobsen's method and also increasing the magnitude of the effects observed for a given amount of radium C.

Principle of the Method.

The principle of the method adopted in the present experiments is identical with that due to Jacobsen, but the dimensions of the apparatus were fixed so that for a given source of radium C four times as many α-particles would be obtained in these experiments as in his work. Since it is essential to obtain as efficient a recoil as possible, the source of radium C must be prepared with great care, avoiding all traces of tarnishing and surface contamination.

A number of unsuccessful experiments was made with Von Lerch's method, using a nickel plate on which to deposit the radium C; but it was found that the best surface was obtained by depositing the radium C on a piece of platinum foil by electrolysis. This method of preparing a source of radium C is quite efficient and so the details of the method, which was worked out under the direction of Dr. R. G. Dickinson, of the Pasadena Institute, California, are given below, as it does not appear to have been used before.

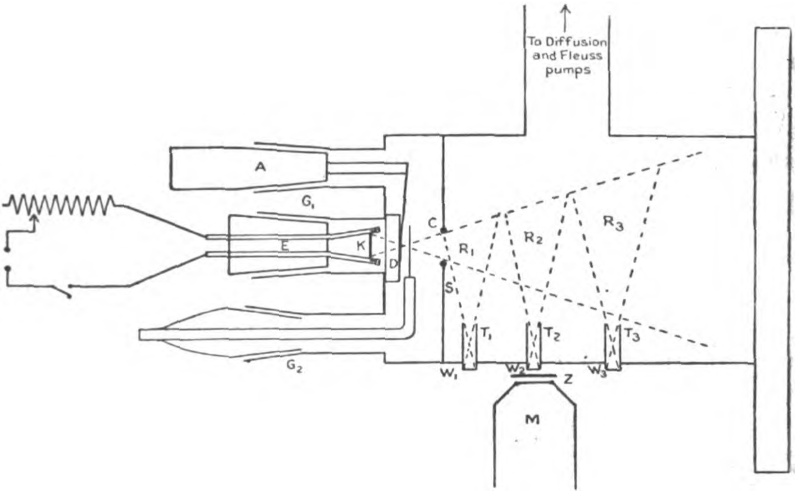
Preparation of the Source of Radium C.

Radium active deposit is obtained on the walls of a thin glass tube by exposing it to radium emanation for four hours, after which the tube is broken up and the active deposit is dissolved in about 5 c.c. of 20 per cent. hydrochloric acid. The platinum foil, 2 mm. × 6 mm., on which the radium C is to be deposited, dips into this solution and forms the cathode of a voltameter, the anode being in a separate vessel. After allowing 25 minutes for most of the radium A to decay away, the solution is heated to 80° C. and stirred by rotating the cathode itself, and the electrolysis is then started. The value of the current is adjusted so that the P.D. between the cathode and a calomel electrode in 20 per cent. hydrochloric acid is not numerically greater than $-0{\cdot}4$ volt. If this value is exceeded, a sensible amount of radium B is deposited on the cathode. The electrolysis is allowed to proceed for 10 mins., when the cathode is removed from the solution, the current being switched off by this removal itself; otherwise a considerable amount of radium C would go into solution again, owing to the cathode being left for a short time in the hot hydrochloric acid with no current flowing. The source is then washed in distilled water and dried by a clean filter-paper; the surface of the platinum shows no trace of tarnish whatever and is as clean and bright as at the commencement of the electrolysis. Under these conditions a source of radium C containing only $\frac{1}{2}$ per cent. of radium B can be obtained, as much as 60 per cent. of the radium C present in the solution being obtained on a piece of platinum foil of the above dimensions. It is essential that the volume of the solution of the active deposit be not greater than about 5 c.c. and that the P.D. between the cathode and the calomel electrode should be numerically less than $-0{\cdot}4$ volt.

The Experiments to Determine the Half-Period of Radium C.

The apparatus finally used in these experiments is shown in fig. 2. It consists essentially of a brass box about 6·0 cm. long with a square cross-section, one side being pierced by three tubes T_1, T_2, T_3, each closed by a mica window W_1, W_2, and W_3, respectively. A microscope M carrying a zinc-blende screen Z can be brought opposite any one tube at will, and is used to count the number of α-particles issuing per minute from that tube.

Fig. 2.



The source of radium C prepared as above is screwed to two brass rods passing through the ground ebonite stopper E and inserted in the apparatus, which is then exhausted to a pressure of less than 10^{-4} mm. of mercury by a two-stage diffusion pump backed by a Fleuss pump. At this pressure the mean free path of radium C′ atoms is much greater than 6 cm., and so they can travel to the end of the box without collision. The source is then disconnected from the rest of the apparatus by turning the valve D by means of the ground metal joint A into the position shown, and it is then heated electrically to about 400° C. for some 30 secs. Previous experiments by the author on β-ray recoil have shown that this heating in a vacuum produces the conditions giving maximum efficiency of recoil *.

---

* Phil. Mag. i. p. 835 (1926).

A simple test experiment showed that the valve D, although not absolutely gas-tight, was quite adequate to prevent any serious increase in contamination. The communication between the source and the apparatus being restored, a beam of radium C′ atoms with a constant solid angle defined by a circular hole in the screen S now passes down the apparatus. The average velocity of these atoms is of the order of 10^5 cm. per sec., and assuming that the half-period of radium C′ is 10^{-5} sec., it is evident that the number of atoms in the beam crossing any given plane perpendicular to it in one second is just one half that crossing a parallel plane one centimetre nearer the source in one second. Thus the number of atoms in a given length of the beam decreases rapidly with distance from the source, and the relation between these two quantities is found by counting the number of α-particles per minute impinging on a zinc-blende screen placed in turn opposite the tubes T_1, T_2, and T_3, correcting them for the decay of the radium C source. For the number of α-particles per minute falling on the screen when opposite, say, the tube T_2 is proportional to the number of radium C′ atoms breaking down in the region R_2 and so to the number present in that region. The number of radium C′ atoms in a given region of the beam and the distance from the centre of that region to the source are now known. The latter quantity can be converted into time assuming the velocity of the recoil atoms, and so the decay of radium C′ can be studied and its half-period determined. This method is admittedly not so precise as that due to Jacobsen, since the regions R are bigger than the corresponding regions in his experiments; but the above scheme was adopted in order to increase the effects obtained. The inaccuracy introduced in this way, however, is much less than that due to the variation of the velocity of the recoil atoms, which affects both sets of experiments.

In the present apparatus no α-particles emitted directly from the source K can pass through the tubes T_2 and T_3 without being scattered at least twice, and their velocity would then be insufficient to enable them to penetrate the mica windows W_2 and W_3 of 4 cm. air equivalent closing these tubes. Again, if an α-particle from the source were scattered through a suitable angle, about 90°, at the edge of the circular hole in the screen S, it could pass straight through the tube T_1. But by lining the hole with carbon the velocity of the scattered α-particle corresponds to a range of about 3 cm. of air, and so it cannot penetrate the mica window W of 4 cm. of air equivalent. Thus none of the α-particles counted in these experiments can be due to scattering; this was confirmed by subsidiary experiments.

Finally, it is necessary to know the number of α-particles at each tube due to contamination and any other spurious effects which may have been overlooked. This was determined by rotating a mica screen of 1 cm. air equivalent in front of the source by the ground glass joint G_2. This screen stops the beam of recoil atoms completely, and so any α-particles counted now are due to spurious effects. The number so obtained when subtracted from the number counted with the source uncovered by the screen gives the number of α-particles due to the disintegration of radium C′.

The advantages of these experiments over Jacobsen's method are:

(1) The entire elimination of scattering.

(2) The way in which the number of α-particles due to spurious effects is estimated.

The number of α-particles per min. per mg. of radium C to be expected at T_1 is 20, assuming an efficiency of recoil of 0·5 per cent. As sources up to 5 mgs. were available, it should be possible to obtain quite definite evidence as to the existence and half-period of radium C′.

Results.

The magnitude of the effects obtained in these experiments was not nearly so large as was expected; this was probably due to low efficiency of recoil, as it is impossible to prevent considerable fluctuations in its value. The experiments were still further complicated by contamination, which often masked the effect of radium C′ and rendered many of the experiments inconclusive. Contamination could not be prevented by cutting off the communication between the source and the box by a collodion film, say, for any such film will stop the stream of radium C′ atoms. But a sufficient number of successful experiments was performed to show quite definitely that radium C′ exists and to enable its half-period to be determined.

The existence of radium C′ is proved if the number of α-particles per minute at T_1 is distinctly greater with the source uncovered by the mica screen than when covered. This was found to be the case in nine experiments, the ratio of the number with the source uncovered to that with it covered varying from 2:1 to 5:1. The details of one of these experiments are appended :—

Number of α particles per min.	
Source uncovered.	Source covered.
36	9
22	2
9	3
5	0
9	2

The results of this experiment show quite clearly that radium C′ exists, and this is confirmed by the other experiments. The sudden decrease in the numbers at the third count is due to the fact that a considerable time (about 30 mins.) elapsed between it and the second count, during which observations were being taken at tubes T_2 and T_3.

In most of these experiments contamination at the tubes T_2 and T_3 was relatively so large that no definite conclusions could be drawn as to the existence of radium C′ opposite them, *i. e.* in the regions R_2 and R_3. It must have been there, but the amount was so small as to be masked by the contamination. In two of the experiments, however, the effects were of such a magnitude relative to the inevitable contamination as to enable the half-period of radium C′ to be determined. The details of these experiments are now given :—

Strength of radium C source at beginning of the first count = 9 mgs.

Average number of α-particles counted per min. due to radium C′ corrected for the decay of the radium C source at tubes T_1, T_2, and T_3 = 36, 19, and <3 respectively. (The average of 6 counts at T_1 and T_2, and of 2 counts at T_3.)

Number of radium C′ atoms present in the regions R_1, R_2, and R_3 at any instant = 36, 19, and <3 respectively.

Now the distance from the centre of R_1 to the centres of R_2 and R_3 = 1·0 and 2·5 cm. respectively.

Time taken for radium C′ to move from R_1 to R_2 and R_3 $= 2{\cdot}5 \times 10^{-6}$ sec. and $6{\cdot}0 \times 10^{-6}$ sec. respectively, assuming the velocity of the recoil atoms to be 4×10^5 cm. per sec.

Thus a decay curve may be drawn from the above data:—

Number of Atoms of Radium C′.	Time 10^{-6} sec.
36	0·0
19	2·5
< 3	6·0

The half-period calculated from this curve is $2·7 \times 10^{-6}$ sec. It is unfortunate that no value could be assigned with certainty to the amount of radium C′ in the region R_3. The counts at the tube T_3 were made after those at T_1 and T_2, and the number of α-particles due to radium C′ to be expected was about 4 per min., which was too small to be detected with any certainty. The smallness is due to the decay of the radium C source and to the fact that the centre of the region R_3 is 4 cm. from the source K, from which it follows that the amount of radium C′ leaving the source has decayed to 1/16 of its initial value when it reaches the centre of R_3. This disadvantage of having the region R_3 so far from the source was unavoidable if the size of the regions R_1, R_2, and R_3 was to be increased so as to make the effects obtained in these experiments larger than those in Jacobsen's work.

The value of the half-period obtained from the other experiment is $3·2 \times 10^{-6}$ sec., so that the mean of the two is $3·0 \times 10^{-6}$ sec. This agrees very well with Jacobsen's value, which is $1·5 \times 10^{-6}$ sec., if the velocity of the recoil atoms were taken to be 4×10^5 cm. per sec., as in this work, instead of his value, 8×10^5 cm. per sec. The value, 4×10^5 cm. per sec., was chosen for two reasons. Firstly, Jacobsen's value is the maximum theoretical velocity of the recoil atoms corresponding to an electron emitted with a velocity of 0·998 c. It is quite certain that only a small fraction of the recoil atoms would have this velocity, and so it was discarded; it may also be mentioned that Jacobsen states in his paper that it is a somewhat arbitrary choice. Secondly, the velocity of the recoil atoms varies continuously from 4×10^4 cm. per sec. to 8×10^5 cm. per sec., and it seems most reasonable, therefore, to use the mean value of their velocity in calculating the half-period of radium C′. Now the number of recoil atoms with a given velocity will vary with that velocity in the same way as the number of electrons emitted from radium C varies with their velocity. Using the results obtained by Chadwick and Ellis [*] for this distribution, the mean value of the velocity of the recoil atoms works out to be 4×10^5 cm. per sec.

---

[*] Proc. Camb. Phil. Soc. xxi. p. 274 (1923).

These experiments, then, confirm Jacobsen's work as to the existence of radium C′. Although the observations are not so accurate as Jacobsen's, nor is the method itself so precise, yet the value of the half-period obtained in this work is probably as accurate as his value because of the great inaccuracy introduced by the uncertainty of the velocity of the recoil atoms.

Summary.

The previous work of Fajans and Jacobsen on the existence and half-period of radium C′ is discussed, and the importance of confirming Jacobsen's results is emphasized.

A repetition of Jacobsen's experiments with certain modifications is described.

The result of this work confirms Jacobsen's experiments—that is. radium C′ does exist and its half-period is of the order of 10^{-6} sec.

In conclusion I should like to express my sincere thanks to Prof. Sir Ernest Rutherford, O.M., P.R.S., for suggesting this problem and for his advice and encouragement while it was being carried out. I have to thank Mr. R. A. R. Tricker, Trinity College, Cambridge, for his assistance in the counting of the *α*-particles. I am indebted to Mr. G. A. R. Crowe for preparing the Radium Active Deposit used in these experiments.

CXXV. *The Loud-Speaker as a Source of Sound for Reverberation Work.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I HAVE recently read a paper by Dr. A. H. Davis and Mr. N. Fleming, entitled "The Loud-Speaker as a Source of Sound for Reverberation Work," published in your issue for July 1926, and should be glad of the opportunity of commenting upon it so far as concerns two references to a work of my own, viz. "On the Degradation of Acoustical Energy," Proc. Roy. Soc. A, vol. cv. pp. 80, &c. (1924).

Dr. Davis deduces from his elegant experimental work the conclusion that appreciable degradation does not exist within the particular range of frequencies and intensities which he investigated. The process of reasoning whereby he arrives at this conclusion is peculiar and interesting. In effect he says, correctly enough (pp. 55–57), "If I employ a microphone of constant sensitivity throughout its range of response and *if there be no degradation*, then two particular curves,which I shall take, should theoretically be of the same form."

He then continues, "I tried three microphones: The first two yielded curves of different forms, so that I discarded them; but the third did give me the two curves alike. *Therefore this microphone is of constant sensitivity, and further, as a necessary corollary, there is not any degradation.*"

As a matter of fact, there is good reason to suppose that the sensitivity of the type (electrostatic) of microphone in question decreases with increase of the effect which it indicates, and it is easy to see that the sense of this deviation is such as would tend to counterbalance degradation effects, and thus to render the two curves in question of the same shape. Dr. Davis apparently consents to this view so far as the microphone is concerned, as he impliedly acknowledges the tendency of the microphone response curve to deviate from the linear when he says (p. 53): "The e.m.f. generated by the electrostatic microphone is, for small amplitudes, directly proportional to the amplitude; . . ." It is noteworthy that a "small" amplitude remains undefined, being presumably that for which the response of the microphone is linear, although personally I prefer to regard it as one at which degradation is negligible.

I refrain from further comment on the paper as a whole, as it does not elsewhere refer explicitly to work of my own, but I should like to call attention to the whole of the paragraph on page 58, commencing "In the present experiment . . . ." and ending ". . . . position of the microphone." In particular, the last two lines of the paragraph—"Thus, in all cases the e.m.f. gives a measure of the sound amplitude at the position of the microphone"—are, to my mind, merely a statement of what one means by a microphone.

I remain,
Yours faithfully,
MORRIS HART.

Air Defence Experimental
Establishment, Biggin Hill,
Westerham, Kent.
3rd November, 1926.

CXXVI. *Notices respecting New Books.*

The Progress of Atomic Theory. By Dr. A. C. Crehore. (Taylor & Francis. 12*s.* 6*d.* net.)

THE appearance of this collected account of a certain mode of envisaging the problem of atomic structure is welcome, as is any serious attempt made, even at the present day, to interpret the phenomena in a manner more in line with the classical electrodynamics. In fact, although the models here discussed are, of course, not reconcilable with those postulated in the present form of quantum theory, it is nevertheless of interest to know the results to which they lead when certain premises are applied from the start. The author is a very competent mathematician, and can be relied upon at all points to find the strict logical consequences of the starting-points of his investigations. Thus, even to the convinced supporter of the quantum foundation, the book will be found to be of value and to suggest much for thought, whether viewed as a thesis investigating further ways in which the classical theory can suggest possible models capable of covering certain restricted domains of experience, or looked upon with the intention of comparison with the advancing quantum. The printing and general form of the book reflect great credit on the publishers, and misprints seem to be extremely rare.

The Thirteen Books of Euclid's Elements. By T. L. Heath. (Second Edition. Cambridge University Press, 1926. 3 volumes. £3 10*s.* 0*d.* net.)

The present volumes constitute a second edition of the thirteen books of Euclid's Elements translated from the text of Heiberg, with an introduction and commentary by Sir Thomas Heath. The first edition appeared in 1908 and was received with great enthusiasm by a large body of readers.

It is admitted that Heiberg's text is by far the best. To his admirable translation Sir Thomas added elaborate notes, sometimes historical, sometimes geometrical. The result of his tremendous labours has been the appearance of the present comprehensive work. The second edition now under review has been very carefully revised, many paragraphs are re-written, and sometimes even a sequence of paragraphs. Several additions have been made, and perhaps the most interesting is the use of much new matter in the two Excursuses at the end of vol. 1, dealing with, in the first place, Pythagoras and the Pythagoreans, and secondly, popular names for Euclid's individual proportions, founded on such things as the shape of the figures drawn by Euclid to illustrate them. An immense amount of research work must have been involved in getting such material together even for a few pages of text.

The same remark is true of the rest of the book, which is packed even more closely than before with paragraphs in smaller print, containing the most interesting historical information accessible nowhere else to English readers. In fact, distinguished as he is so uniquely as a mathematician and Greek scholar combined, the author is nevertheless a very remarkable historian. In the preface he lays stress on the fact that Euclid is the greatest mathematical work which has come to us in the past, quite apart from the question as to how it should be taught, or how such matters as the Axiom of Parallels should be treated. We should like to say that these three volumes will themselves long remain classical, for they have given us all that can be found from any source on the far history of one branch of mathematics, and in a critical manner of the deepest research.

It is hardly necessary to say that the printer's share in the publication is beyond praise, for the Cambridge University Press never deviates from the high standard of all the mathematical works it issues.

Projective Geometry. By C. V. DURELL. (Macmillan & Co., 1926.)

THIS volume is a sequel to the author's 'Modern Geometry,' which deals with the properties of triangles, pencils, and circles. It is an abbreviated form of 'A Course of Plane Geometry for Advanced Students, Part II.,' published in 1910. Certain re-arrangements of the material have been made, and a considerable number of riders have been added. The book indeed contains a very ample supply of riders which will make it especially valuable.

We shall look forward to welcoming the author's projected work, 'A Concise Geometrical Conics.' There is at present great need of a well-written book on this subject.

Solutions of the Examples in a Treatise on Dynamics of a Particle and of Rigid Bodies. By S. L. LONEY, M.A. (Cambridge University Press, 1926. 17*s.* 6*d.* net.)

THE present work consists of solutions to the examples in Professor Loney's well-known Treatise. No doubt a not inconsiderable number of those teachers and students who use this text-book will be glad to have at hand for reference the solutions as given. It should be particularly useful for those students who have to work alone, though for this class of reader the solutions may sometimes prove rather too sketchy.

Photographic Photometry. By G. M. B. Dobson, I. O. Griffith, and D. N. Harrison. (Oxford, Clarendon Press. 7*s*. 6*d*. net.)

This work is described as a study of methods of measuring radiation by photographic means. The old description of books as supplying a long-felt want can be applied with complete truth to this volume. Much of the work described has been the outcome of research investigations in the Clarendon Laboratory, in some cases very recent, and on the part of the writers themselves. It has, therefore, a strong meteorological bent; and this fact constitutes one of its real values, for it is in this department that most striking new photometric work is being mainly done at the present time. The list of those who have assisted the three authors, mentioned in the Preface, is a final guarantee that the work is completely authoritative everywhere. We can recommend it with confidence as a work which should rapidly prove essential to the library of any experimental physicist, and equally to the teacher of Physics whether in a School or University. Its outlook is physical, and not mathematical, throughout.

The form of the volume, as it leaves the Press, is very pleasing, and the Oxford University Press is to be congratulated on such an addition to its list.

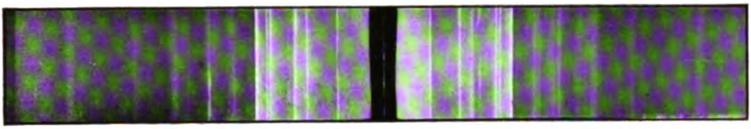
Early Medicine and Biological Sciences. By R. T. Gunther, (Oxford University Press (Mr. Humphrey Milford), 1926. Pp. 247. 8vo. 7*s*. 6*d*. net.)

This volume is part of the author's larger book on 'Early Science in Oxford,' and has been re-issued by request without the plates so as to bring its cost within the reach of a larger number of students.

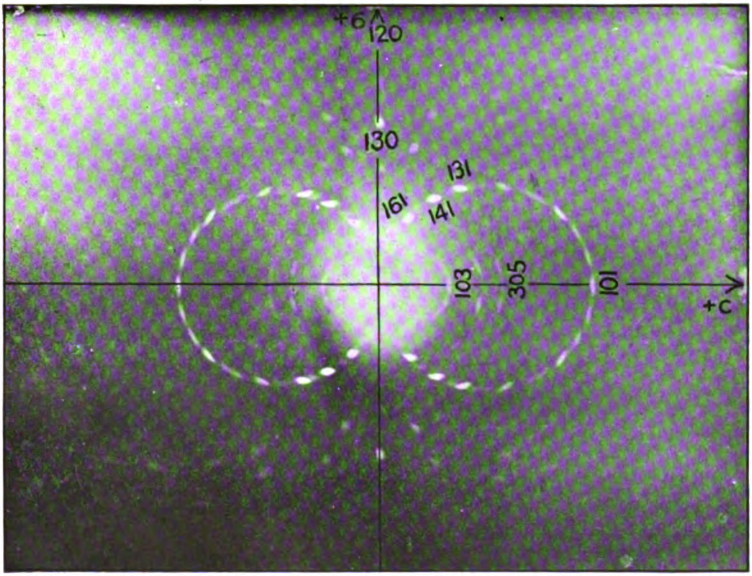
The work deals with early Medicine. Anatomy, Physiology, Zoology, Botany, and Geology, and though replete with historical data, is well and interestingly written. It is packed full of curious and out-of-the-way learning, and contains many striking illustrations and a few topical poems.

The story of Oxford's illustrious geologists introduces us to Hooke, Plot and his Theory of Fossils, Edward Lhwyd, "Strata Smith," Buckland (two poems and a picture describing his lectures), Sedgwick, Merchison, the great Lyell, and others—an imposing list of great masters of whom Oxford has a right to be proud.

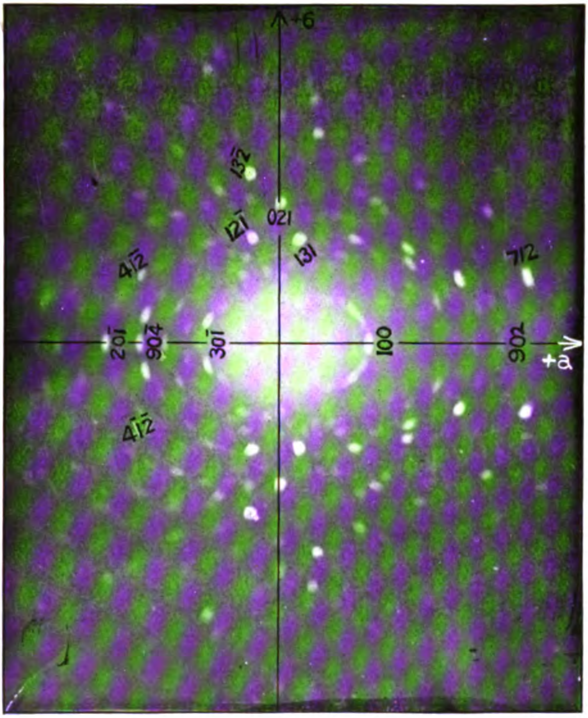
This is a book which will appeal both to scholars and to dilettanti; it is both learned and amusing.



Catechol. 3·48 cm.



Potassium Ferricyanide : *a* (100) face. 4 cm.



Aluminium Acetylacetone : *c* (001) face. 4 cm.

CXXVII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 750.]

May 5th, 1926.—Dr. F. A. Bather, F.R.S., President. in the Chair.

THE following communication was read:—

'The Geology of the District around Towyn and Abergynolwyn (Merioneth).' By Ralph Maurice Jehu, M.Sc., F.G.S.

The area investigated includes about 35 square miles of country, lying south-west of the Corris district, which has been recently described.[1] The rocks belong to the Bala and Valentian Series, and consist mainly of mudstones and shales with subordinate bands of grit. The lithological and faunal characters of the rocks are, on the whole, similar to those around Corris, so that the same classification and the same nomenclature have been retained so far as possible. The rocks of the Bala Series are described in detail.

The mapping of the various subdivisions has revealed the detailed structure of the area. The district is situated on the south-eastern flank of the Harlech Dome, so that, in general, the strata strike from south-west to north-east, and dip south-eastwards; but the area is crossed transversely by large anticlinal and synclinal folds, the axes of which trend north-north-eastwards in the south, and become north-and-south farther north. These transverse folds cause considerable deviation in the outcrops of the various rock-groups, and, within the major folds, there is evidence of minor folding.

The Bala or Tal-y-llyn Fault runs from south-west to north-east through the area, and is marked by the straight, steep-sided Tal-y-llyn Valley. There can be little doubt that this is a tear-fault with comparatively little vertical displacement; but, at present, it is impossible to state with any degree of precision the actual amount of lateral and vertical displacement. On the north side of the fault some seven main fold-axes have been recognized by Prof. A. H. Cox,[2] while on the south the author describes four main fold-axes. Difficulty is experienced when an attempt is made to correlate the structures on each side of the fault-line.

The southern part of the area is much affected by faulting, and three main groups of faults may be recognized: namely, (1) an east-and-west group; (2) a north-east and south-west group; and (3) a north-west and south-east group.

The rocks are highly cleaved, and the extraction of fossils is thereby rendered difficult. The strike of the cleavage-planes is approximately from south-west to north-east.

[1] W. J. Pugh, Q. J. G. S. vol. lxxix (1923) p. 508.

[2] Q. J. G. S. vol. lxxxi (1925) p. 576.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

INDEX TO VOL. II.

ACOUSTIC measurements, on the basis of, by reverberation methods, 543.

Adeney (Dr. W. E.) on the aeration of water under open-air conditions, 1140.

Air, on the Joule-Thomson effect for, 961; on the rate of solution of, in water, 1140.

Alkalis, on the magnetic susceptibilities of some, 21.

Alloys, on the thermoelectric properties of, 1188.

Alty (S.) on the effect of tension on the elastic properties of wires, 321.

Aluminium amalgams, on the conductivity of, 19.

—— acetylacetone, on the crystal structure of, 1161.

Amalgams, on the resistivity and conductivity of dilute, 1; on the effect of a magnetic field on the resistance of, 176.

Andrews (J. P.) on an application of diffraction halos to elasticity, 945.

Anemometer, on the vane, 881.

Anhydrite, on the crystalline structure of, 114, 992.

Annular nozzles, on eddying flow from, 436.

Anodic polarization, on, 733.

Antimony amalgams, on the conductivity of, 17.

Arc, on the high vacuum, in hydrogen, 796.

—— spectrum of potassium, on the, 1042.

Argon, on the scattering of positive rays by, 1076.

Atoms, on the distance between, in crystals, 258; on the electrical structure of, 1026.

Baker (J. F.) on the stresses in a spoked wheel under loads applied to the rim, 1234.

Banister (Dr. H.) on the transmission of sound through the head, 144; on the phase-effect and the localization of sound, 402.

Barkas (W. W.) on the photophoresis of colloidal particles in aqueous solutions, 1019.

Barkla (Prof. C. G.) on scattered X-rays and the J phenomenon, 642, 1116, 1122.

Barrel of an air-cooled cylinder, on temperature stresses and deflexions in the, 449.

Barton (A. W.) on the existence and half-period of radium C, 1273.

Bath for observations at low temperatures, on a, 383.

Beals (C. S.) on the spectrum of ionized silver, 770.

Benzoic acid, on the molecular association of, in benzene, 287.

Beryllium amalgams, on the conductivity of, 19.

Beta-rays, on the ranges of secondary, 1109.

Biggs (H. F.) on a simple exposition of electromagnetic relations, 1052.

Binks (W.) on the crystalline structure of anhydrite, 114.

Binnie (A. M.) on temperature stresses and deflexions in the fins and barrel of an air-cooled cylinder, 449.

Bircumshaw (L. L.) on the surface tension of liquid metals, 341.

Björnståhl (Y.) on electric double refraction in colloids, 701.
Books, new:—Crehore's The Progress of Atomic Theory, 1284; Jolly's Summation of Series, 496; Kaye & Laby's Four-Figure Mathematical Tables, 496; Bose's The Nervous Mechanism of Plants, 496.
Bowen (I.) on the effect of tension on the elastic properties of wires, 321.
Boys type of double resonator, on the, 751.
Bragg (Prof. W. L.) on interatomic distances in crystals. 258.
Bridgman (P. W.) on dimensional analysis, 1263.
Briggs (Dr. S. C.) on Werner's coordination theory and the electrical structure of the atom, 1026.
Browning (Dr. H. M.) on sound changes analyzed by records, 955.
Cadmium, on the structure of the resonance lines of, 611; on the fine structure of certain lines and energy levels of, 613.
Cæsium, on the magnetic susceptibility of, 21.
Calcium sulphate, on the crystalline structure of anhydrous, 114, 992.
Campbell (Dr. N. R.) on the variation of pressure with temperature in evacuated vessels, 369.
Carroll (M. F.) on molecular association and the equation of state, 385.
Cassen (B. M.) on the striated distribution of space charge, 948.
Catechol, on the crystal structure of, 1153.
Cathode, on the effect of the shape of the, on the glow discharge, 556.
—— rays, on the radiation produced by, 678.
Cerium amalgams, on the conductivity of, 18.
Chadwick (Dr. J.) on the artificial disintegration of elements, 1056.
Chaplin (R.) on the adsorption of nitrogen at low pressures by activated charcoal, 1198.
Charcoal, on the adsorption of nitrogen by, 1198.
Circuits, on the general formulæ for two syntonized coupled, 1098; on the resistance of high-frequency, 1213.
Clark (Dr. L. H.) on secondary radiations produced by gamma-rays, 783.
Cohen (B. S.) on the condenser-telephone, 1271.
Colloidal particles, on the photophoresis of, in aqueous solutions, 1019.
Colloids, on electric double refraction in, 701.
Compton effect and the reflexion of X-rays by crystals, on the, 657.
Condenser, on the parallel plate, 827.
Condenser-telephone, on the, 497, 1271.
Continuous medium in four-dimensional space, on the equilibrium and motion of a, 994.
Convergence of series, on the relation to physics of the notion of, 241.
Coordination compounds, on the atomic structure and magnetic properties of, 86.
—— theory, on Werner's, 1026.
Copper, on the X-ray spectrum of, 1011; on the thermoelectric properties of solid solutions of, 1188.
—— spectrum, on the analysis of the, 194.
Coupled circuits, on the general formulæ for two syntonized, 1098.
Crystal lattice of metallic elements, on the, 1148.
—— structure of certain compounds, on the, 1153.
Crystals, on interatomic distances in, 258; on the deformation of tungsten, 289; on the reflexion of X-rays by, 657.
Daniell (Dr. P. J.) on orthogonal potentials, 247.
Dauvillier (Dr. A.) on the electric discharge in gases, 1046.
Davies (Dr. A. C.) on critical potentials and X-ray term values, 1253.
Davis (Dr. A. H.) on the loud-speaker as a source of sound for reverberation work, 51; on the basis of acoustic measurements by reverberation methods, 543.

Density of fluids, on the, 1127.
Dickson (Dr. E. C. S.) on the crystalline structure of anhydrite, 114.
Dickson (T. W.) on the oblique rebound of a ball from a plane, 1091.
Diffraction halos, on an application of, to elasticity, 945.
Dimensional analysis, on, 1263.
Disintegration of elements, on the artificial, 1056.
Dobson, Griffith and Harrison's Photographic Photometry, 1286.
Donaldson (R. H.) on a new method of obtaining a luminous discharge in gases at low pressures, 129, 742.
Double refraction, on electric, in colloids, 701.
Durell's Projective Geometry, 1285.
Earth, on the surface history of the, 245, 1218.
Eckersley (T. L.) on the Compton scattering and the structure of radiation, 367.
Eclogite, on, as the substratum of the earth's crust, 1230.
Eddies, on the growth of, in a viscous fluid, 844.
Eddying flow from annular nozzles, on, 436.
Edwards (E.) on the effect of tension on the elastic properties of wires, 321.
Edwards (T. I.) on the resistivity and conductivity of dilute amalgams, 1.
Ehrenhaft (Prof. F.) on the determination of the size and weight of submicroscopic spheres, 30.
Elastic material, on a geometrical presentment of the constants of an, 588.
—— properties of wires, on the effect of tension on the, 321.
—— range of friction, on the, 806.
Elasticity, on the determination of the modulus of, by dynamical methods, 351; on an application of diffraction halos to, 945; on the coefficients of, for the solid state, 431.
Electric discharge in gases, on the, 913, 1046.
—— double refraction in colloids, on, 701.
Electric resistance, on the, at fusion and the crystal lattice of metallic elements, 1148; on the, of high-frequency circuits, 1213.
Electrical structure of the atom, on the, 1026.
Electricity, on the radiation produced by the passage of, through gases, 674.
Electrolytes, on the Milner and Debye theories of strong, 577, 586.
Electromagnetic relations, on a simple exposition of, 1052.
Electrons and molecules, on the transference of energy in collisions between, 474.
Elements, on the artificial disintegration of, 1056.
Elles (Dr. G. L.) on the geology of Ben Lawers, 749.
Elliptic functions, on two-dimensional fields specified by, 827.
Engine cylinder, on the temperature stresses and deflexions in an air-cooled, 449.
Equation of state, on molecular association and the, 385.
Ethyl chloride, on the latent heat of vaporization of, 817.
Eumorfopoulos (N.) on the Joule-Thomson effect for air, 961.
Evacuated vessels, on the variation of pressure with temperature in, 369.
Evans (Dr. J.) on regions of compression, 748.
Explosions, on the shape of waves from large, 137.
Fearnsides (Prof. W. G.) on the Cambrian slate-belt of Nantlle, 744.
Fins of an air-cooled cylinder, on temperature stresses and deflexions in the, 449.
Fleming (N.) on the loud-speaker as a source of sound for reverberation work, 51.
Flickers, on the theory of, in vision, 1170.
Flow, on irrotational, past two intersecting planes, 900.
Fluids, on the stability of layers of, heated below, 833; on the growth of eddies in viscous, 844; on the density of, 1127.

Focken (C. M.) on the transference of energy in collisions between electrons and molecules, 474.
Four-dimensional space, on the equilibrium and motion of a continuous medium in, 994.
Friction, on the elastic range of, 806.
Gamma-rays, on secondary radiations produced by, 783.
Gases, luminous discharge in 743, 1272.
——, on a new method of obtaining a luminous discharge in, at low pressures, 129, 741, 742, 743; on the scattering of light in, 237; on the residual, in evacuated vessels, 369; on the transference of energy in collisions between electrons and molecules in, 474; on the high-frequency oscillatory discharge in rarefied, 508; on the radiation produced by the passage of electricity through, 674; on the electric discharge in, 1046; on the scattering of positive rays by, 1076.
Geological Society, proceedings of the, 744, 1287.
Germanium amalgams, on the conductivity of, 15.
Gill (E. W. B.) on a new method of obtaining a luminous discharge in gases at low pressures, 129, 742.
Glenday (V. G.) on the geology of the Suk Hills, 744.
Glow discharge, on the effect of the shape of the cathode on the, 556.
Gold, on the properties of colloidal, 38; on the arc spectrum of, 208; on electric double refraction in, 715; on the thermoelectric properties of solid solutions of. 1188; on the atomic structure of compounds of, and zinc, 1266.
—— particles, on the size of colloidal, 1024.
Goucher (F. S.) on the deformation of tungsten single crystals, 289.
Granites, on the pre-Cambrian, 1218.
Gravity, on the action in parabolic paths under, 800.
Gray (Dr. R. C.) on the magnetic stability of permanent magnets, 521.
Green (Dr. G.) on the condenser-telephone, 497.
Grumbach (Prof. A.) on the origin of the E.M.F. of a photoelectric cell, 313.
Guggenheim (E. A.) on the velocity constant of a unimolecular reaction, 538.
Gunther's Early Medicine and Biological Sciences, 1286.
Gwyther (R. F.) on a geometrical presentment of the constants of an elastic material, 588.
Halos, on an application of diffraction, to elasticity, 945.
Hart (M.) on the loud-speaker as a source of sound for reverberation work, 1282.
Hartley (H.) on the Milner and Debye theories of strong electrolytes, 586.
Haze, on the making of a salt, 1165.
Head, on the transmission of sound through the, 144.
Heat, on the nature of, 1006.
Heath's The thirteen Books of Euclid's Elements, 1284.
Helium, on absorption and resonance radiation in excited, 529; on the scattering of positive rays by, 1076.
Hicks (Prof. W. M.) on the analysis of the copper spectrum, 194.
High-frequency circuits, on the resistance of, 1213.
High resistances, on the calculation and application of, of small self-inductance, 65.
Holmes (Dr. A.) on the radioactivity of potassium and its geological significance, 1218.
Horton (Prof. F.) on critical potentials and X-ray term values, 1253.
Houstoun (Dr. R. A.) on the theory of the absorption of X-rays, 512.
Howland (R. C. J.) on the oblique rebound of a ball from a plane, 1091.
Hughes (Dr. E.) on the minimization of magnetic leakage, 162.
Hydrochloric acid, on the activity coefficients of aqueous, 1085.
Hydrogen, on a new method of producing a discharge in, 743; on the high vacuum arc in, 796.

Hydrogen line, on self-reversal of the red, 876.
Integraph, on a simple, 778.
Interatomic distances in crystals, on, 258.
Iron, on the water-spark absorption spectrum of, 742; on the thermoelectric properties of solid solutions of, 1188.
Irrotational flow past two intersecting planes, on, 900.
J phenomenon, on the, 642, 1116, 1122.
Jackson (Dr. L. C.) on the atomic structure and magnetic properties of coordination compounds, 86.
Jeffreys (Dr. H.) on the relation to physics of the notion of convergence of series, 241; on the stability of a layer of fluid heated below, 833.
Jenkins (H. G.) on the nitrogen afterglow spectra, 621.
Jehu (R. M.) on the geology of the district around Towyn and Abergynolwyn, 287.
Johnson (Mrs. M. R.) on intensity variations in the spectrum of neon, 593.
Johnson (Dr. R. C.) on intensity variations in the spectrum of neon, 593 on the nitrogen afterglow spectra, 621.
Joly (Prof. J.) on the surface history of the earth, 245.
Jones (Miss P.) on the effect of a magnetic field on the resistance of mercury and some amalgams, 176.
Jones (T. J.) on the effect of a magnetic field on the resistance of mercury and some amalgams, 176.
Joule-Thomson effect for air, on the, 961.
Kasterin (Prof. N. P.) on Sir J. J. Thomson's model of a light-quantum, 1208.
Khastgir (Dr. S. R.) on scattered X-rays, 642.
Kirchner (Dr. F.) on a new method of obtaining a luminous discharge in gases at low pressures, 741; on the luminous discharge in an alternating field, 1272.
Kirkby (Rev. P. J.) on alternative currents in rarefied oxygen in the same circuit, 913.
Kunz (Dr. J.) on the scattering of light in gases, 237.
Lasareff (Prof. P.) on the theory of flickers in peripheral and central vision, 1170.
Latent heats of vaporization of ethyl and methyl chlorides, on the, 817.
Lawson (Dr. R. W.) on the radioactivity of potassium and its geological significance, 1218.
Lead, on the surface tension of liquid, 341; on the arc spectrum of, 633.
Legendre function of order —½, on the, 1184.
Levy (Prof. H.) on the growth of eddies in a viscous fluid, 844.
Light, on the scattering of, in gases, 237.
—— quantum, on a simple, 1157; on Sir J. J. Thomson's model of a, 1208.
Loney's Solutions of the Examples in a Treatise on Dynamics of a, Particle and of Rigid Bodies, 1285.
Loud-speaker, on the, as a source of sound for reverberation work, 51, 1282.
Lowry (H. V.) on the Legendre function of order —½, 1184.
Luminous discharge in gases at low pressures, on a new method of obtaining a, 129, 741, 742, 743, 1272.
Lunt (Dr. R. W.) on the current voltage characteristic of a Siemens ozonizer, 314; on a new method of producing a discharge in hydrogen, 743.
Lyman (Prof. T.) on an improved grating for vacuum spectrographs, 310.
McCurdy (Dr. W. H.) on absorption and resonance radiation in excited helium and the structure of the 3889 line, 529.
Mackenzie (Miss G. I.) on scattered X-rays, 1116.
Magnesium, on the atomic structure of compounds of silver and, 1266.
Magnetic field, on the effect of a, on the electrical resistance of mercury and some amalgams, 671.
—— leakage, on the minimization of, 162.

Magnetic properties of coordination compounds, on the, 86.
—— spectrum method of investigating X-ray levels, on the, 1262.
—— susceptibilities of some alkalis, on the, 21.
Magnets, on the magnetic stability of permanent, 521.
Marr (Prof. J. E.) on the pleistocene deposits of the Ouse basin, 750.
Meksyn (D.) on the equilibrium and motion of a continuous medium in four-dimensional space, 994.
Mercury, on the resistivity and conductivity of, 1; on the effect of a magnetic field on the electrical conductivity of, 176; on electric double refraction in, 713.
—— still, on a simple vacuum arc, 317.
Merton (Prof. T. R.) on reversal in vacuum tube spectra, 975.
Metallic elements, on the electric resistance at fusion and the crystal lattice of, 1148.
Metals, on the surface tension of liquid, 341.
Methyl chloride, on the latent heat of vaporization of, 817.
Molecular association and the equation of state, on, 385.
Molecules, on the transference of energy in collisions between electrons and, 474.
Morris (T. O.) on the Cambrian slate-belt of Nantlle, 744.
Morton (Prof. W. B.) on the action in parabolic paths under gravity, 800; on the parallel-plate condenser, 827; on irrotational flow past two intersecting planes, 900.
Neon, on intensity variations in the spectrum of, 593.
Newman (Prof. F. H.) on the high vacuum arc in hydrogen, 796; on the flash arc spectrum of potassium, 1042.
Nickel, on the X-ray spectrum of, 1011; on the thermoelectric properties of solid solutions of, 1188.
Nitrogen on the afterglow spectra of, 621; on the rate of solution of, in water, 1140; on the adsorption of, by activated charcoal, 1198.
Nonhebel (G.) on the Milner and Debye theories of strong electrolytes, 566; on the activity coefficients of dilute hydrochloric acid, 1085.
Norbury (Dr. A. L.) on the thermoelectric properties of metallic solid solutions, 1188.
Nozzles, on eddying flow from annular, 436.
Nuttall (J. M.) on the ranges of secondary beta-rays, 1109.
Oblique rebound, on the, of a ball from a plane, 1091.
Orifice flow as affected by viscosity and capillarity, on, 852.
Orthogonal potentials, on, 247.
Oscillations, on relaxation, 978.
Oscillatory discharge in rarefied gas, on the high frequency, 508.
Oxygen, on alternative currents in rarefied, in the same circuit, 913; on the scattering of positive rays by, 1076; on the rate of solution of, in water, 1140.
Owen (Dr. E. A.) on the atomic structure of AgMg and AuZn, 1266.
Owens (Dr. J. S.) on the making of a salt haze, 1165.
Ower (E.) on the vane anemometer, 881.
Ozonizer, on the current voltage characteristic of a Siemens, 314.
Palladium, on the thermoelectric properties of solid solutions of, 1188.
Parabolic paths, on the action in, under gravity, 800.
Particle and of Rigid Bodies, Dynamics of a, 1285.
Paris (Dr. E. T.) on the "Boys" type of double resonator, 751.
Parkinson (J.) on the geology of the Suk Hills, 744.
Patterson (W. H.) on a bath for observations at low temperatures, 383.
Perlitz (Dr. H.) on the electric resistance at fusion and the crystal lattice of metallic elements.
Permeameter, on a modified form of the Iliovici, 162.
Phase effect and the localization of sound, on the, 402.

Phosphor-bronze wires, on the effect of tension on the elastic properties of, 321.

Photoelectric action, on the distribution of energy among the electrons emitted from a plate by, 680.

——, on the origin of the E.M.F. of a, 313.

—— emission from platinum, on the, 463.

Photophoresis of colloidal particles in aqueous solutions, on the, 1019.

Physics, on the relation to, of the notion of convergence of series, 241.

Pippard (Prof. A. J. S.) on the stresses in a spoked wheel under loads applied to the rim, 1234.

Planes, on irrotational flow past two intersecting, 900.

Platinum, on the photoelectric emission from, 463; on the thermoelectric properties of solid solutions of, 1188.

van der Pol (Dr. B., jr.) on relaxation oscillations, 978.

Polarization, on anodic, 733.

Positive column in oxygen, on the, 913.

—— rays, on the radiation produced by, 678; on the scattering of, by gases, 1076.

Potassium, on the magnetic susceptibility of, 21; on the flash arc spectrum of, 1042; on the radioactivity of, 1218.

—— ferricyanide, on the crystal structure of, 1156.

Potentials, on orthogonal, 247; on critical, and X-ray term values, 1253.

Press (Prof. A.) on the elasticity coefficients and the thermodynamic integration factor for the solid state, 431.

Pressure, on the variation of, with temperature in evacuated vessels, 369.

Preston (G. D.) on the atomic structure of AgMg and AuZn, 1266.

Quantum, on Sir J. J. Thomson's model of a light-, 1208.

Radiation, on the Compton scattering and the structhre of, 267; on the, produced by the passage of electricity through gases, 674.

Radioactivity of potassium and rubidium, on the, 1218.

Radium C, on the half-period of, 1273.

Rai (J.) on the Joule-Thomson effect for air, 961.

Ramsey (Prof. R. R.) on the resistance of high-frequency circuits, 1213.

Rankin (J. S.) on the elastic range of friction, 806.

Reaction, on the velocity constant of a unimolecular, 538.

—— constant equation, on the, 448.

Rebound, on the oblique, of a ball from a plane, 1091.

Relaxation oscillations, on, 978.

Resistances, on the calculation and application of high, of small self-inductance, 65.

Resonance lines, on the, of cadmium and zinc, 611.

—— radiation of excited helium, on the, 529.

Resonator, on the Boys type of double, 751.

Reverberation methods, on the basis of acoustic measurements by, 543.

—— work, on the loud-speaker as a source of sound for, 51, 1282.

Reversal in vacuum tube spectra, on, 975.

Richards (R. C.) on the high-frequency oscillatory discharge in rarefied gas, 508.

Richardson (Dr. E. G.) on eddying flow from annular nozzles, 436.

Robb (Dr. A. A.) on a simple integraph, 778.

Rubidium, on the magnetic susceptibility of, 21; on the radioactivity of, 1218.

Salt haze, on the making of a, 1165.

Sarkar (Dr. A. N.) on an X-ray examination of the crystal structure of certain compounds, 1153.

Scatchard (G.) on the Milner and Debye theories of strong electrolytes, 577.

Searle (V. H. L.) on an oscillographic study of anodic polarization, 733.

Self-reversal of the red hydrogen line, on, 876.

Series, on the relation to physics of the notion of convergence of, 241.
Shand (Prof. J.) on the geology of Pilansberg, 747.
Shaxby (Dr. J. H.) on the density of fluids, 1127.
Sheppard (S. E.) on the reaction constant equation, 448.
Siemens ozonizer, on the current voltage characteristic of a, 314.
Silver, on the arc spectrum of, 207; on the spectrum of ionized, 770; on the thermoelectric properties of solid solutions of, 1188.
Silver, on the atomic structure of compounds of, and magnesium, 1266.
Sodium, on the magnetic susceptibility of, 21.
—— chloride, on electric double refraction of, 727.
Solid solutions, on the thermoelectric properties of, 1188.
Sound, on the transmission of, through the head, 144; on the phase-effect and the localization of, 402.
—— changes analyzed by records, 955.
Space charge, on the striated distribution of, 948.
Spectra, on reversal in vacuum tube, 975; on the X-ray, of the lower elements, 1007.
Spectrographs, on an improved grating for vacuum, 310.
Spectrum, on the analysis of the copper, 194; on intensity variations in the, of neon, 593; on the afterglow, of nitrogen, 621; on the arc, of lead, 633; on the, of ionized silver, 770; on the flash arc, of potassium, 1042.
Stability of a layer of fluid heated below, on the, 833.
Stephenson (W.) on the effect of the shape of the cathode on the glow discharge, 556.
Still, on a simple vacuum arc mercury, 317.
Stoner (Dr. E. C.) on X-ray term values, absorption limits, and critical potentials, 97.
Stresses in a spoked wheel, on the, 1234.
Striated distribution of space charge, on the, 948.
Submicroscopic spheres, on the determination of the size and weight of, 30.
Sucksmith (W.) on the magnetic susceptibilities of some alkalis, 21.
Sulphur, on electric double refraction in, 722.
Sur (A. K.) on the water-spark absorption spectrum of iron, 742.
Sur (N. K.) on the arc spectrum of lead, 633.
Surface tension of liquid metals, on the, 341.
Sutton (T. C.) on the shape of waves from large explosions, 137.
Swift (H. W.) on the determination of the modulus of elasticity by dynamical methods, 351; on orifice flow as affected by viscosity and capillarity, 852.
Telephone, on the condenser-, 497, 1271.
Thallium amalgams, on the conductivity of, 10.
Thermodynamic equation of state, on the, 431.
Thermoelectric properties of metallic solid solutions, on the, 1188.
Thomson (Prof. G. P.) on the scattering of positive rays by gases, 1076.
Thomson (Sir J. J.) on the radiation produced by the passage of electricity through gases, 674.
Thoræus (R.) on the X-ray spectra of the lower elements, 1007.
Tin, on the surface tension of liquid, 341.
Townsend (Prof. J. S.) on the transference of energy in collisions between electrons and molecules, 474.
Tungsten single crystals, on the deformation of, 289.
—— wires, on the effect of tension on the elastic properties of, 321.
Tyler (E.) on eddying flow from annular nozzles, 436.
Ultraviolet light, on the production of real images of submicroscopic particles by means of, 30.
Unimolecular reaction, on the velocity constant of a, 538.

Vc

Vacuum spectrographs, on an improved grating for, 310.
—— tube spectra, on reversal in, 975.
Vanadium, on the X-ray spectrum of, 1007.
Vane anemometer, on the, 881.
Velocity constant of a unimolecular reaction, on the, 538.
Violin, analysis of the sounds of the, 955.
Viscous fluid, on the growth of eddies in a, 844.
Vision, on the theory of flickers in, 1170.
Voice, analysis of the sounds of the, 955.
Waran (Prof. H. P.) on a simple vacuum arc mercury still, 317.
Wasastjerna (Prof. J. A.) on the crystalline structure of anhydrite, 992.
Wasser (Dr. E.) on the determination of the size and weight of submicroscopic spheres, 30.
Water, on the aeration of, under open-air conditions, 1140.
Watson (Dr. W. H.) on the control of the J phenomenon, 1122.
Waves, on the shape of, from large explosions, 137.
Welo (Dr. L. A.) on the photoelectric emission from platinum, 463.
Werner's coordination theory, on, 1026.
Wheel, on the stresses in a spoked, 1234.
Whittaker (Prof. E. T.) on a simple light-quantum, 1137.
Wilcken (Dr. J. A.) on the molecular association of benzoic acid in benzene, 287.
Williams (E. J.) on the Compton effect and the reflexion of X-rays by crystals, 657; on the ranges of secondary beta rays, 1109.
Wilmotte (R. M.) on high resistances of small self-inductance, 65; on general formulæ for two syntonized coupled circuits, 1098.
Wires, on the effect of tension on the elastic properties of, 321.
Wood (Prof. R. W.) on an improved grating for vacuum spectrographs, 310; on the structure of cadmium and zinc resonance lines, 611; on the self-reversal of the red hydrogen line, 876.
X-ray examination of the crystal structure of certain compounds, on the, 1153.
—— spectra of the lower elements, on the, 1007.
—— term values, on, 97, 1253.
X-rays, on the theory of the absorption of, 512; on scattered, 642, 1116, 1122; on the reflexion of, by crystals, 657; on the nature of soft, 1050.
Yates (G. W. C.) on the latent heats of vaporization of ethyl and methyl chlorides, 817.
Yttrium amalgams, on the conductivity of, 18.
Zinc, on the atomic structure of compounds of gold and, 1266.
——, on the X-ray spectrum of, 1011.
—— resonance lines, on the structure of, 611.

END OF THE SECOND VOLUME.

Printed by TAYLOR and FRANCIS, Red Lion Court, Fleet Street.

DATE DUE

11-20-84			

GAYLORD PRINTED IN U.S.A.

PX 000 783 784

C 4- 22 A

DATE DUE

11-20-84			

GAYLORD PRINTED IN U.S.A.

PX 000 783 784
C 4- 22 A

DATE DUE

11-20-84			

GAYLORD PRINTED IN U.S.A.

PX 000 783 784

C 4- 22 A